Modification chimique de surface de NanoFibrilles de Cellulose (NFC)

Karim Missoum

UNIVERSITÉ DE GRENOBLE

THÈSE

Pour obtenir le grade de

DOCTEUR DE L'UNIVERSITÉ DE GRENOBLE

Spécialité : **Matériaux, Mécanique, Génie Civile, Electrochimie**

Arrêté ministériel : 7 août 2006

Présentée par

Karim MISSOUM

Thèse dirigée par **Mohamed Naceur BELGACEM**
codirigée par **Julien BRAS**

préparée au sein du **Laboratoire du Génie des Procédés Papetiers de l'Ecole Internationale du Papier de la Communication Imprimée et des Biomatériaux, UMR CNRS 5518**

dans **l'École Doctorale Ingénierie – Matériaux, Mécanique, Energétique, Environnement, Procédés de Production**

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Pr. Etienne FLEURY
Professeur de l'INSA Lyon, Président
Dr. Monika ÖSTERBERG
Maître de Conférences de l'Université d'Aalto (Finlande), Rapporteur
Pr. Stéphane GRELIER
Professeur de l'Université de Bordeaux 1, Rapporteur
Pr. Mohamed Naceur BELGACEM
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Remerciements

Remerciements

Tout d'abord, je tiens à remercier vivement les membres du jury d'avoir examiné et participé à ma soutenance de thèse ce qui m'a valu le titre de docteur. Etienne Fleury, professeur à l'INSA Lyon, j'ai été honoré de votre présence et merci d'avoir accepté la présidence du jury, ceci était une vraie volonté de vous avoir dans le comité de lecture de ma thèse. *It was also a pleasure to count Monika Österberg, associated professor in Aalto University (Finland), as one reviewer of my work. Your expertise in the domain of chemical modification of NFC was really appreciated; your remarks, advices, works of your team were helpful during my PhD. Thanks again!! Hope to see you again in the "small world" of cellulose.* J'ai également été ravi de rencontrer Professeur Stéphane Grelier de l'Université de Bordeaux. Vos remarques pertinentes ont été appréciées et ont permis une compréhension certaine sur les propriétés antibactériennes. Je remercie le Docteur Noël Cartier pour son point de vue industriel et son regard sur les faisabilités des procédés développés pour une utilisation à plus haute échelle.

I would like also to thank all the European project partners. All of you, at different level, have contributed to a good achievement of my work and allow getting a real expertise in NFC field. Firstly, I would to make a special thanks to Ulla (VTT) and Tiemo (PTS), project coordinator and the "module 2" referee respectively, for your advices during this 3 last years, to allow presenting my work for the two SUNPAP workshop and SUNPAP meetings. It was really helpful to manage my "stress". Thank you Patrizia and Graziano (Innovhub, ex SSCCP) the Italian partners for the different discussions, advices, analyses etc etc… Patrizia I'm still waiting my pizza!!!! ☺. I also thank all the French "mafia" from CTP / FCBA, Sandra et Denilson (en premier lieu qui m'ont été d'une aide non négligeable durant ces trois ans merci à vous deux !). Ne vous inquiétez pas Florence, Céline, BenJ et Valérie je vous mets aussi dans la boucle pour les nombreuses phases de rire durant les déplacements, ça aurait été bien moins funky sans vous… Stop talking French!. Thank you to Nanosight partner (Bob & Agnieszka) for their help in characterization, Karita from VTT, Menno from Ahlström for their motivation and for have used our products. Prof. Lars Järnström for its kind remarks, stories, advices. I'm sure I forgot a lot of partners and I apologize. I want to express my gratitude to all of you; it was a nice project with a lot of challenges, hoping to see some of you in future collaborative projects. Thanks again!!

Maintenant on va passer à des choses bien plus sérieuses le labo !!! Ci-dessous une liste non exhaustive (ah si en fait elle l'est :D) des personnes que j'ai été ravi de rencontrer, avec qui j'ai pu partager de bons moments, des mauvais, des coups de gueules etc… :

Juste avant ça un énorme merci à Francine et Stéphane pour leur sympathie et leur disponibilité! (Mes genoux me font encore mal :D) !

Le service technique (Xav, Oliv', Lolo, Chu, ma charlotte !!) toujours un bonjour, une blague (parfois pas drôle hein Lolo) mais toujours de bonne humeur et souriant ça fait du bien !

Bertine (pour les pauses clopes), Nevin (pour les pauses clopes), Bertrand et Lucie (pour les pauses clopes) … si si on bosse quand même un peu entre deux ! Pas beaucoup mais on bosse :D. Merci à tous ceux qui suivent pour le soutien et/ou juste des discussions, franche rigolade, les coups de gueule, (ou juste parce qu'ils sont sympa !!! L'ordre n'est pas une préférence mais la suite logique des bureaux quand on entre à l'école c'est plus simple) : Fred, Nevin, Momo, Nathalie. L, Ahlem, Denis, La Rattaz, Stéphane (Alias Dufduf), Agnès, Céline. M, Patrice, M-C B.S), Pierre, Lucie (encore)… (L'étage du bas est fini on passe en haut) David, Karine, Awatef, Alain. D, Bertrand (encore), Raphael. B, Florian (de m'avoir supporté en PFE), Didier, Ramzi, Julien (on y reviendra), Naceur (tout pareil que Julien), Mickael, Cécile (alias Mme de Casse-c*******), Beth, JFK, José, Christian… (Attention on arrive dans la vallée des rois = bureaux où il y a la clim !!!!) MA TANTINE (Bureau dans lequel j'ai surement du passer autant de temps que dans les labos… tu avais raison tu vas partir à la retraite que je serai encore là!!!!), Isabelle, Nathalie, Isabelle, Evelyne, … On fait demi-tour direction l'imprimerie … Tonton Jean-Luc, Franck, Anne, Nadège … Et voilà ceci termine le tour du labo et de son personnel (privé/public comme ils aiment à dire) avec qui j'ai apprécié perdre du temps.

Des personnes exceptionnelles qui sont plus des amis que des chefs ou des mini-chefs comme j'aime à les appeler. Naceur tes conseils pendant ces dernières années ont été très précieux aussi bien au niveau professionnel que personnel ! MERCI CHEF ! Julien (mini-chef), merci pour toute la patience dont tu as su faire preuve avec ce petit sale gosse que je suis (étais), j'ai (presque) arrêté de râler :D. L'aventure continue … ! « Avis aux lecteurs si vous voulez réaliser une thèse avec deux chefs de folie, qui sont juste les meilleurs dans le labo, un combo parfait, Envoyez Naceur et Juju au 3 15 15 (numéro non surtaxé !!) (ca va ne soyez pas jaloux les autres :D) »

D'autres belles rencontres qui sont devenus de vrais potes, Gilberto, Bertrand, Aurore et ma Débo !! Je vous souhaite le meilleur pour l'avenir. Des discussions, des fous rires je

pouvais râler tranquillement avec vous c'était génial !!! Ces rencontres m'ont permis de connaitre d'autres personnes génialissimes ! Merci pour ça !

D'un point de vue plus privé, Nelly, Solène, Marlou (alias mes trois bi*ches :D), Steven, Ben, Nico, Ben2, Adrien, Aurèl, Math, JP, Steph…!!! Bon bah vous savez de quoi il en retourne toujours à répondre présent quand il le faut !!!! Vous êtes juste au top !

Un grand merci à ma famille (trop long à citer 48 personnes) ! Merci maman, merci papa, ma grand-mère, Soso, Sabrina, à ma nièce Meïssanne, ma « poupée », Nass… comme on dit on choisit ses amis mais pas sa famille … pour rien au monde j'en changerai !

Je commence à fatiguer, les effusions de sentiments ne sont pas mon fort ! On va donc s'arrêter là. La plus part des gens savent ce que je pense d'eux, les remerciements sont sympas mais pas besoin de grand discours pour leurs dire tout ça ! Ils le savent déjà : je vous aime !!

Pour conclure un ENORME MERCI à tous ceux qui ont contribué de près ou de loin à ce succès et qui seront encore présent pour de nombreuses années je l'espère ! Un chapitre qui se ferme un autre qui s'ouvre …

A tous mes proches « Famille & Amis »

" Le vrai bonheur ne dépend d'aucun être, d'aucun objet extérieur. Il ne dépend que de nous."

" La meilleure façon de prédire l'avenir, c'est de le créer. " Peter Drucker

" Donne à manger à un chien, il te chie dans la main. " Karim :D

Scientific Publications (2009 – 2012)

Scientific Journals

1. Karim Missoum, Mohamed Naceur Belgacem, Jean-Paul Barnes, Marie-Christine Brochier-Salon, Julien Bras, *Nanofibrillated Cellulose surface grafting in ionic liquid*, **Soft Matter**, 8 (32), 8338–8349 (**2012**).

2. Karim Missoum, Mohamed Naceur Belgacem, Julien Bras. *Organization of aliphatic chains grafted on nanofibrillated cellulose and influence on final properties*. **Cellulose**, 19 (6), 1957–1973 (**2012**).

3. Karim Missoum, Julien Bras, Mohamed Naceur Belgacem. *Water Re-dispersible Dried Nanofibrillated Cellulose*. **Biomacromolecules** 13 (12), 4118-4125 (**2012**).

4. Karim Missoum, Mohamed Naceur Belgacem, Julien Bras. *Effect of chemically modified NanoFibrillated Cellulose addition on the properties of fiber-based materials*, **Industrial Crops and Products**, 48, 98-105 (**2013**).

5. Karim Missoum, Mohamed Naceur Belgacem, Julien Bras. *Nanofibrillated Cellulose surface modification: A review.* "Advances in Cellulosic Materials" **Materials**, 6(5), 1754-1766 (**2013**).

6. Karim Missoum, Mohamed Naceur Belgacem, Florian Martoïa, Julien Bras. *All-Cellulose bionanocomposites: cellulose derivatives reinforced with nanofibrillated cellulose*, Submitted to **Composites – Part A: Applied Science and Manufacturing** (**2013**).

7. Karim Missoum, Mohamed Naceur Belgacem, Julien Bras. *Biodegradability assessment and antimicrobial activity of nanofibrillated cellulose* Accepted in **Materials science engineering C** (**2013**).

Patent - Brevet (2009 – 2012)

1. Karim Missoum, Mohamed Naceur Belgacem, Julien Bras. Déposé le *25 juin 2012* : *Procédé de fabrication d'une poudre de cellulose fibrillée adaptée à être dispersée en milieu aqueux*, Number : FR12/55997

2. Karim Missoum, Mohamed Naceur Belgacem, Julien Bras. Déposé le *25 juillet 2013* : *Procédé de formation d'une couche hydrophobe*, Number : Obtention d'un film hydrophobe

Oral Communications in Scientific Meeting

1. Missoum, K.; Belgacem, M. N.; Bras, J. *AKD nano-emulsions: Innovative technique to increase the solid content of NFC suspensions*, Workshop June 2012 Milan Italy (Oral Communication)

2. Missoum, K.; Belgacem, M. N., Bras, J. *Surface chemical modification of nanofibrillated cellulose in ionic liquids*. Abstracts of Papers, 243rd ACS National Meeting & Exposition, San Diego, CA, United States, March 25-March 29, 2012 (2012), CELL-201 (Oral communication)

3. Missoum, K.; Belgacem, M. N.; Bras, J. *Nanofibrillated cellulose surface grafting in ionic liquid,* Workshop September 2011 Espoo Finland (Oral Communication)

4. Julien Bras, Karim Missoum, Nathalie Lavoine, Artur Klamczynski, Isabelle Desloges, Naceur Belgacem, William J Orts, Alain Dufresne. *Different nanofibrillated cellulose and innovative strategies developed for their uses in coating or extrusion*. ISWFPC conference 2011, 16th International Symposium on Wood, Fiber and Pulping Chemistry, Tianjin (Chine), 8-10 juin 2011, paper 407 (Oral Communication)

5. Missoum, K., Belgacem, M. N., Krouit, M., Martin, C., Tapin-Lingua, S., Bras, J. *Influence of fibrillation degree & surface grafting of micro-fibrillated cellulose on their rheological behavior in aqueous suspension***.** International Conference on Nanotechnology for the Forest Products Industry 2010; Otaniemi, Espoo; 28-29 September 2010. Pages 326-350. (Oral Communication)

Posters in International Conference

1. Missoum, K.; Belgacem, M. N., Mauret, E.; Bras, J. "*Determination and comparison of the charge of different nanofibrillated cellulose*". Abstracts of Papers, 243rd ACS National Meeting & Exposition, San Diego, CA, United States, March 25-March 29, 2012 (2012), CELL-91 (Poster)

2. Karim Missoum, Déborah Le Corre, Alain Dufresne, Naceur Belgacem, Céline Martin, Julien Bras**.** "*Rheological behavior of different bio-based nanoparticles suspensions*". International Conference on Nanotechnology for the Forest Products Industry 2010; Otaniemi, Espoo; 28-29 September 2010. (Poster)

Abbreviations

AFM	Atomic Force Microscopy
AKD	Alkene Ketene Dimer
CA	Cellulose Acetate
CAB	Cellulose Acetate Butyrate
CAP	Cellulose Acetate Propionate
DMA	Dynamic Mechanical Analysis
DP	Degree of Polymerization
DS	Degree of Substitution
DSC	Dynamic Scanning Calorimetry
DSS	Degree of Substitution of Surface
E-NFC	NFC obtained by enzymatic pretreatment
ESEM	Environmental Scanning Electron Microscopy
FE-ESEM	Environmental Scanning Electron Microscopy Equipped with a Field Emission Gun (FEG)
FE-SEM	Scanning Electron Microscopy Equipped with a Field Emission Gun (FEG)
FTIR	Fourier Transformed Infra-Red
IL	Ionic Liquid
MFC	MicroFibrillated Cellulose
NaCl	Sodium Chloride
NaOH	Sodium Hydroxide

NCC	NanoCrystalline Cellulose
NFC	NanoFibrillated Cellulose
NFC_AA	NFC chemically modified with Acetic Anhydride
NFC_BA	NFC chemically modified with Butyric Anhydride
NFC_HA	NFC chemically modified with Hexanoic Anhydride
NFC_i-BA	NFC chemically modified with iso-Butyric Anhydride
NMR	Nuclear Magnetic Resonance
SEM	Scanning Electron Microscopy
TEMPO	2,2,6,6 tetramethyl-1-piperidinyloxy
TGA	Thermo-Gravimetric Analyses
T-NFC	NFC obtained by TEMPO pretreatment
ToF-SIMS	Time of Flight - Secondary Ions Mass Spectrometry
XPS	X-ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction

General Introduction

General Introduction

Europe is still at the moment the most attractive market place for paper and its derivative products. In order to increase growth, the European paper industry has to beat the product commoditization trap and renew its product base with more value-added products to gain competitive advantage against the low-cost producers in emerging countries.

Moreover, consumers demand for bio-based, recyclable and/or biodegradable products is increasing strongly. This is why even if bio-based polyolefin are being developed; waste management and end of life will still be selective parameters. Indeed, the idea is to develop new wood-based products with higher properties than those reached currently in order to increase competiveness of Europe regarding emerging countries. That is why Europe gave founding for three years R&D cycle research in this field which has led to **SUNPAP** project birth (**S**cale-**U**p of **N**anoparticles in modern **PAP**making).

The European SUNPAP project addresses the strengthening of paper industry competitiveness by using nanocellulose based process to provide radical product performance improvements, new efficient manufacturing methods and the introduction of new added value functionalities.

Nano**F**ibrillated **C**ellulose (**NFC**) is the most promising nano-material for wide applications in papermaking or composite for instance. However, today it is only prepared and applied in lab-scale. Also, some main targets of SUNPAP project are to:

- Develop and up-scale a novel process for the production of NFC limiting the energy production consumption.
- *Develop and up-scale NFC modification processes to address the challenges of papermaking and to provide new added-value active functionalities limiting the use of organic solvent.*

**Extracted from Description of work of SUNPAP project*

In the framework of the project, NFC was involved to implement new bio-based products. Our task consisted in development of 3 innovative strategies for chemical modification of NFC and selected one of them for up-scale phase.

A cellulose fibril called NanoFibrillated Cellulose (NFC), with dimension between 5 and 50 nm for diameter and several micrometers in length, are described as long flexible nano-filaments composed of crystalline and amorphous part.

They are obtained after a strong mechanical shearing applied on cellulose slurry which is pump trough a homogenizer or grinder device. Comparing to cellulose fiber-based suspension, NFC displayed higher specific area which leads to a higher amount of hydrogen interactions and as a consequence a gel-like structure at very low solid content (2-5%). NFCs are mechanically interesting due to their high Young modulus equivalent to Kevlar

$$(E_{wood} < E_{aluminium} < \mathbf{E_{NFC}} \approx \mathbf{E_{kevlar}} < E_{carbon\ nanotubes}).$$

Regarding literature available, subject dealing with NFC are daily increasing in spite wide terminologies are used to speak about cellulose nanofibrils. Updated from Lavoine et al. 2012, Figure 1 presents all terminologies employed in scientific papers and their corresponding number of publication per year since 1993 up to end of September 2012.

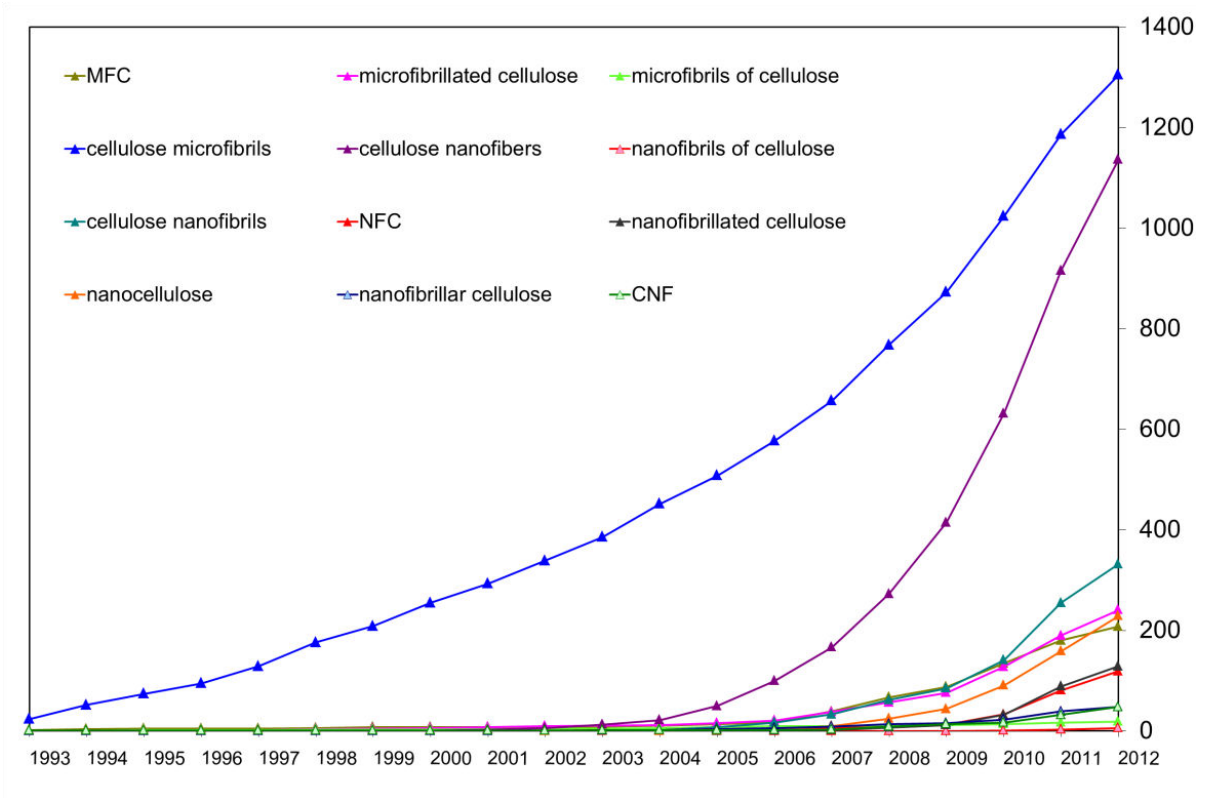


Figure 1 : Cumulative scientific document (papers, review and patent) for the period 1993/01-2012/09 from SciFinder data base

As shown in Figure 1, an exponential interest for NFC starts just few years ago at the beginning of the project. This project is then very interesting and can be considered as a pioneer in the field.

More precisely, this PhD study is involved in a specific WorkPackage (WP5) dedicated to the chemical surface modification of NFCs with the following targets:

- Development of hydrophobic NFC suspensions in order to increase the solid content of the material suspension.
- Development of NFC-based products with active properties for special papers.

The chemical surface modification of NFC is then very innovative and can be one route to answer all the previous questions

Also it is interesting to firstly:

(i) Well understand the raw material used for this project (Chapter 1)

(ii) Adapt existing procedure for chemical grafting and then develop new processes for chemical grafting in non-toxic solvents or using water based process and develop new methods for characterization (Chapter 2)

(iii) Propose some applications using the previous chemically modified NFC (Chapter 3)

Thus, the manuscript was organized in three chapters as presented in Figure 2.

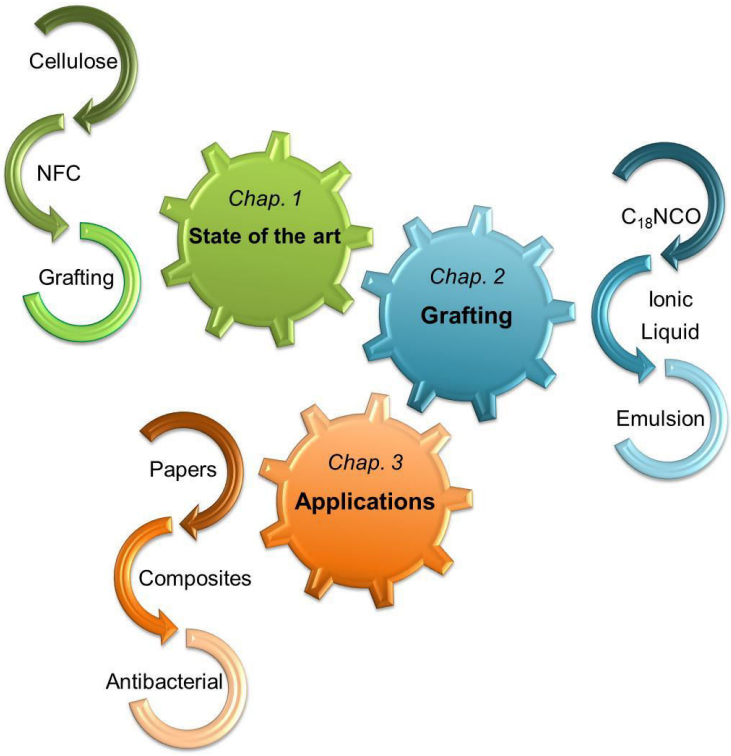


Figure 2 : Manuscript organization

Chapter 1 allows identifying the main challenges to overcome before developing new procedure of chemical grafting onto NFC.

Chapter 2 aims to develop new process in order to chemically modify the surface of NFC. Three main strategies have been followed: either using carbanilation reaction (Paper 1) or esterification based on anhydride reaction within ionic liquid medium (Paper 2) or modification using a process in aqueous media (Paper 3) but not detailed in this manuscript due to patenting in progress.

Chapter 3 assesses the potential use of neat and modified NFC in several applications like papermaking applications (Paper 4), or all-cellulosic composites (Paper 5) or new application in antibacterial activity (Paper 6).

Chapters are mainly based on scientific papers in order to present a homogeneous manuscript. All chapters are tightly linked to each other. Consequently, we hope that the complete manuscript and studies inside bring a global comprehension and potential applications of modified NFC.

All promising results achieved during this study enhance interests onto NFC but also assess new challenges and perspectives. Some of them have also been achieved during this PhD and have been developed in appendix. Indeed **Appendix** 1 is dedicated to a drying method in order to re-disperse NFC in water once dried (Patent and Paper 7).

In conclusion, before any considerations, we should start with a literature review presenting the state of the art of such nanocellulosic materials.

Chapter I.

Literature review

Chapter I.

1. Cellulose

1.1 Chemical structure

Cellulose is the most abundant biopolymer produced in earth. According FAO structure (http://faostat.fao.org 2012), there is approximately 10^{11} – 10^{12} tons of cellulose annually produced by photosynthesis. As early as in 1838, Anselme Payen (1795-1871), a French chemist, established that the fibrous component of all higher plant cells had a unique chemical structure which he named cellulose. He first discovered and isolated cellulose from green plants. Cellulose is also produced by some algae, bacteria, fungi and animal tunicates. The macromolecular structure of cellulose was established in 1930 (Freudenberg et al. 1932; Freudenberg and Blomqvist 1935), and revealed that cellulose is a polymer composed of glucose units.

Glucose is a hexose, i.e. a six atoms hetero-ring. In the conventional representation (Fisher representation), the carbon atoms are numbered from 1 to 6 (Figure I-1). Carbon 1 is the potentially aldehydic carbon (when located as end group), and carbon 6 is the carbon atom standing out of the chain. In this form, the sugar is called a pyranos, giving to glucose its formal name: glucopyranose. Both α and β forms of glucose exist. The form α has its –OH group attached to the carbon 1 above the ring, on the same side as the carbon 4, whereas β has the same –OH group below the ring (Figure I-1)(Stewart 1974). It could have either a boat or chair form but the chair form is more stable. Also, a C1 conformation where the hydroxyl groups lie nearly in the ring plane (equatorial hydroxyls) is preferred.

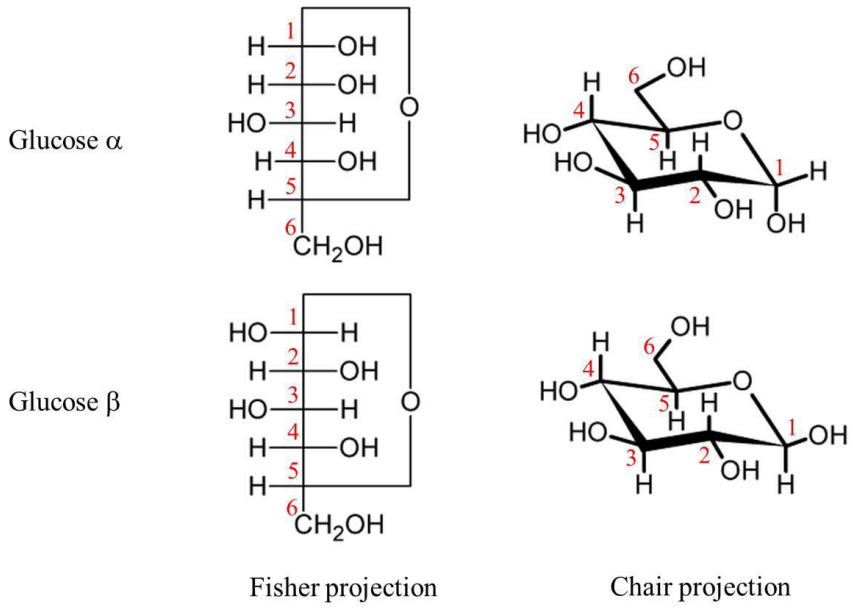


Figure I-1 : Fisher and chair representation of glucose α and β form

When two hydroxyl groups are attached to the carbons (C1 or C4) of two glucose rings come sufficiently close in the presence of the appropriate enzyme, a C-O-C group can be formed and a water molecule is expelled. This reaction is also referred as condensation. The link is called α or β depending on whether the hexoses are in the α or β form. Usually the β form leads to less labile molecules compared to the α form. The condensation reaction between two glucopyranoses in their β form leads to the creation of a C1-O-C4 link and the disaccharide cellobiose. This link is annotated as the β-1,4-link. The creation of cellobiose requires the tilting of one of the glucose units for stereo-chemical reasons (Figure I-2).

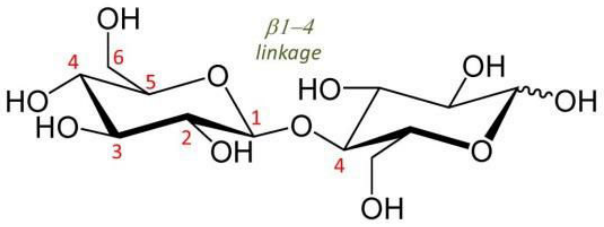


Figure I-2 : Chemical structure of cellobiose unit

Then, cellulose is a linear polymer of D-anhydroglucopyranose units linked together by β−1,4-glucosidic bonds. This conformation gives each molecule a flat ribbon-like structure. Cellulose is also very stable due to this β-1-4-link that is reinforced by an intramolecular hydrogen bond between the ring oxygen atom and the C3 hydroxyl group of the adjacent molecule (Figure I-3). Intermolecular hydrogen bonds are also found between the hydroxymethyl group oxygen and C2 hydroxyl group. The equatorial positions of the glucopyranose residues stabilize the structure of cellulose, increasing its rigidity and resulting in extensive intra and intermolecular hydrogen bonding that also causes insolubility in water. The existence of this bond for the crystalline states has been proven by both FTIR spectroscopy and X-ray diffraction.

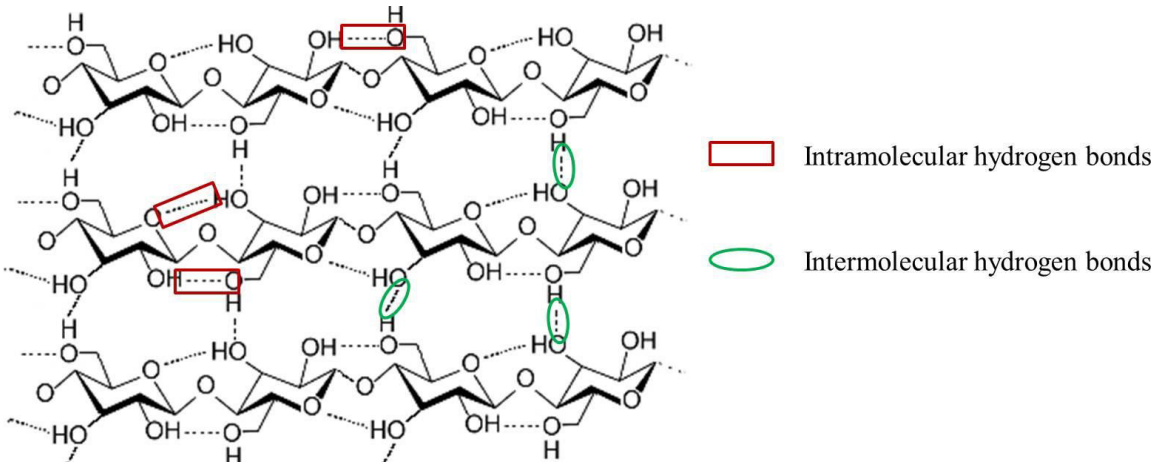


Figure I-3 : Intra and inter molecular hydrogen bonds for several macromolecules of cellulose

According to Sjöström (Sjöström 1993) native cellulose in wood has a degree of polymerization (DP) of approximately 10,000 glucopyranose units and it is around 15,000 for native cellulose in cotton. As reported by Daniel (Daniel 1985) valonia fibers present a DP of 26,500, while cotton fibers present a DP ranging from 20,000 and 14,000 depending on the part of the fiber where the analysis was performed. The DP also varies tremendously from about 20 in the case of laboratory synthetized cellulose to about 4000 for wood (eucalyptus, pines, spruce…) and up to 8000 for ramie (Krässig et al. 2004). Bledzki and Gassan (Bledzki and Gassan 1999) show that purification procedures (namely used in pulp and paper industry) can classically reduce the DP in native cellulose from 14000 to about 2,500. Summaries of typical DPs are available in the literature (e.g. (Krässig et al. 2004)). Cellulose chains are highly hydrophilic due to the presence of large numbers of hydroxyl groups. In the natural state, approximately 40 to 70 of these chains are held together via O6-O3 hydrogen bonding to form a crystalline fibrous structure having approximately 3 nm in diameter.

1.2 Physical Structures: from cellulose to wood

The cellulose microfibril is the basic structural component of cellulose fibers, formed during the biosynthesis. Actually, the chains of poly-β-(1→4)-D-glucosyl residues aggregate to form a fibril, which is a long thread-like bundle of molecules as shown in Figure I-4.

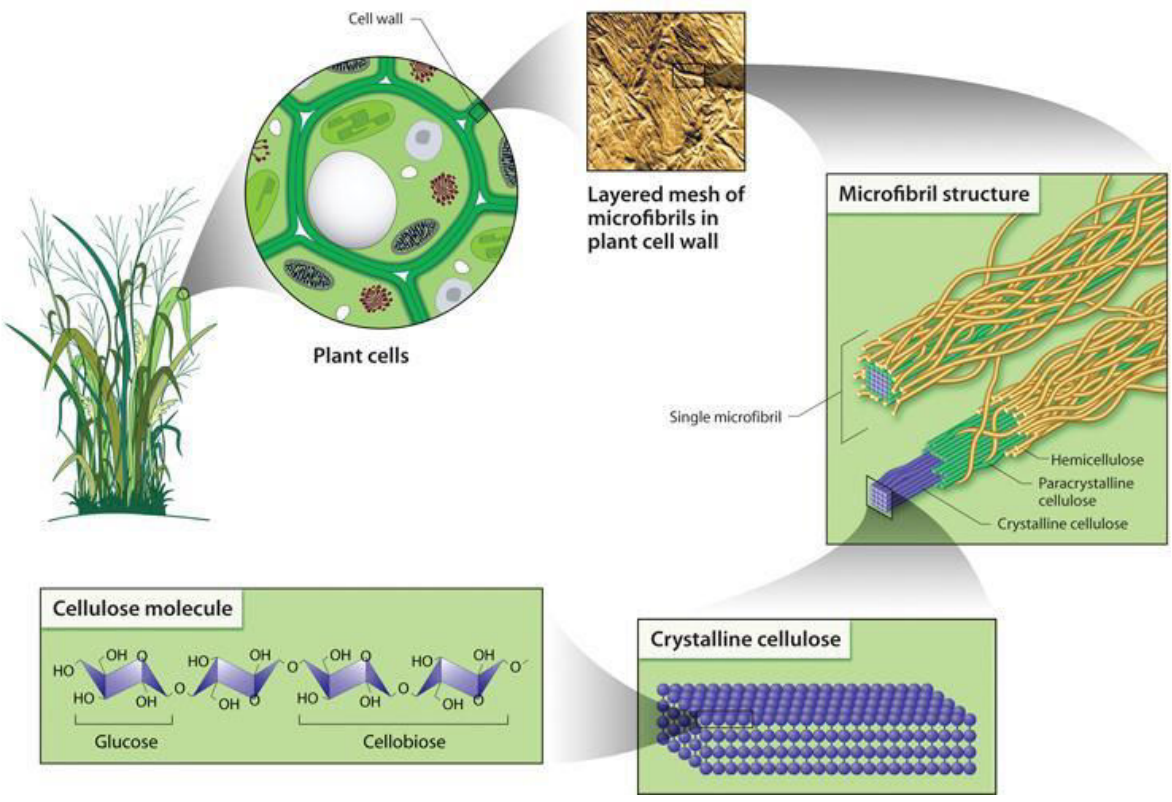


Figure I-4 : From plant to macromolecular chain of cellulose (taken from Siquiera Gilberto PhD)

Individual cellulose microfibrils or nanofibrils have diameters ranging from 2 to 5 nm depending on the source and pre-treatment applied for their production. Each microfibril can be considered as a string of cellulose crystals linked along the microfibril axis by disordered amorphous domains (e.g. twists and kinks). Infra-red spectroscopy and X-ray diffraction studies of cellulose organization in plants have shown that the main portion of native cellulose is constituted by crystallites with interspersed amorphous regions of low degree of order. A model of a wood cellulose microfibril by Fengel and Wegener (Fengel and Wegener 1989) is shown in Figure I-5. This cross-sectional view shows several elementary fibrils (microfibrils) with a width of 3 nm surrounded by hemicelluloses. A bundle of elementary fibrils combined in a parallel arrangement constitutes the cellulose aggregate (called sometimes micro-fibrillated cellulose, MFC) that has a width of about 30 nm. Although the validity of this model is uncertain, it explains the difference in dimensions of nanofibrillated cellulose (NFC) obtained by different extraction routes and which are *the main raw materials studied during this PhD*.

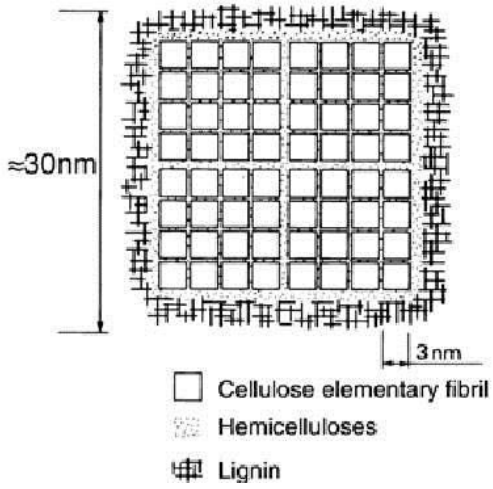


Figure I-5 : Model of cellulose microfibrils proposed by Fengel et Wegener (1989)

Cellulose displays two main polymorphs. Almost all native cellulose consists of cellulose I, i.e. the crystalline cellulose. Cellulose II is used to refer to cellulose dissolved and precipitated (regeneration) or treated with a concentrated alkaline solution and washed with water (mercerization). Indeed cellulose I is not the most stable form of cellulose. An additional hydrogen bond per glucose residue in cellulose II makes this allomorph as the most thermodynamically stable form. The transformation of cellulose I to cellulose II is a subject of interest of many studies since the time when Mercer discovered this transformation in 1850, by submitting native cellulose to a strong alkali treatment. Dinand et al. (Dinand et al. 2002b) have shown that mercerization started as soon as the NaOH concentration became higher than 8% for a sample purified by an acid treatment, and 9% for another resulting from alkaline disencrustation. Moreover, they found that cellulose from the

primary wall presented a higher susceptibility toward aqueous alkali treatment. Such a higher susceptibility may be related to the specific parameters of the primary wall, like the lack of organization and the lateral size of the crystalline microfibrils.

In this project, one key requirement is to keep the native fibrillar morphology and the native crystallinity after any treatment, thus limiting the occurrence of mercerization process. That is why understanding of the dissolution processes and the different cellulose polymorphs is necessary.

1.2.1 Dissolution of cellulose and polymorphs

Dissolution of natural cellulosic materials, followed by cellulose regeneration, has provided more consistent material than can be achieved using natural fibers directly from the field. Features like drapability, coloration potential, texture and tenacity can be tailored for the intended application. Furthermore, the use of cheap wood pulp (with low DP) as a starting material is a cost-effective alternative to high quality natural fibers. Amongst the known processing routes for cellulose dissolution, only a few are used at an industrial scale. The Viscose process was the first of these processes to be discovered and developed at around the turn of the 20th century. Social pressures to seek more eco-friendly alternatives due to the environmental impacts of the Viscose process have been raised in the last decade. Indeed, the Viscose process is a long, complicated, inefficient process. Moreover, it produces sulphur-containing by-products (Chanzy et al. 1990; Krässig et al. 2004).

A dissolution process based on the use of the tertiary aliphatic amine N-oxide hydrates was the subject of extensive research in the seventies. N-methylmorpholine-N-oxide (NMMO) is now successfully used as an organic solvent in an industrial process that produces spun cellulosic fibers under the generic name of “Lyocell”. Other dissolution methods have been used with success to produce textile fibers. Cellulose can, for example, be dissolved with LiCl/DMAc to produce high tenacity fibers (Hong et al. 1998; McCormick et al. 1985).

More recently, attention has been focused on a sustainable process taking advantage of the Q-region in the NaOH, (NaOH concentration around 9% and temperature below 4°C) cellulose phase diagram. In the Q region, cellulose can be completely dissolved under certain conditions (Cai et al. 2007b; Cai et al. 2004; Ruan et al. 2006; Ruan et al. 2004). The uses of cellulose dissolution goes beyond fiber spinning and is found in a broad range of applications ranging from sponges to synthesis of cellulose derivatives. Ionic liquids (ILs) have also recently gained much attention due to their high efficiency and non-volatility which makes them relatively safe to work with (Kosan et al. 2008; Swatloski et al. 2002; Turner et al. 2005; Zhang et al. 2005; Zhu et al. 2006). This quite original solvent (in the present

context) will be used in our study and more details about their interaction with cellulose will be given at the end of the present chapter (cf. Chapter 2.3.2).

Other solvents for cellulose include dimethyl sulfoxide/ammonium fluorides (Heinze et al. 2000; Köhler and Heinze 2007), dimethyl sulfoxide/formaldehyde, inorganic complexes like cuprammonium cuene or cadoxene (Turbak et al. 1977), molten salt hydrates such as $LiClO_4/3H_2O$, $ZnCl_2/4H_2O$ or $LiSCN/2H_2O$ (Leipner et al. 2000), metal complexes (Saalwächter et al. 2000), LiOH/urea (Cai et al. 2007a; Cai and Zhang 2005), ethylene diamine/potassium thiocyanate (Frey et al. 2006), NH_4SCN/NH_3 (Frey et al. 1996), N_2O_4-dimethylformaldehyde and concentrated protonic acids (Turbak et al. 1977).

Actually, there are several crystalline arrangements of cellulose. Each one presents a distinctive diffraction pattern. These polymorphs of cellulose are denoted as cellulose I, II, III_I, III_{II}, IV_I and IV_{II} and they can be inter-converted depending on the chemical treatment and source, as shown in Figure I-6.

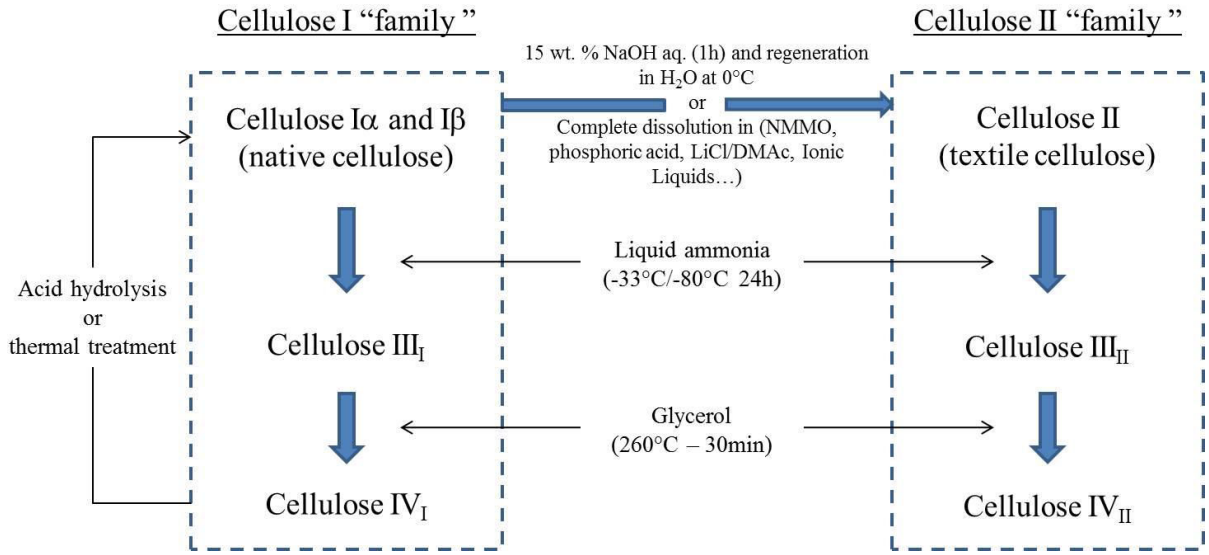


Figure I-6 : Polymorphs of cellulose and inter-connection between them

Crystalline cellulose exists as different allomorphs featuring distinct lattice dimensions, chain orientation and group conformation as summarized in Figure I-6. The distinction between crystalline and amorphous can be made using acid hydrolysis or water sorption in combination with gravimetric methods; it can also be made using spectroscopy tools such as Segal's crystallinity index, Herman's background analysis, and relative absorption bands in infrared spectra or differences in solid-state NMR proton-spin relaxation. However, these techniques provide only a relative gage of the crystallinity. Indeed, it is still quite difficult to quantify the crystalline cellulose *vs.* amorphous counterpart with such experiments which indicate only the crystal quality.

As already said, cellulose is the most abundant biopolymer produced by nature. However only a small amount is used today and most of time this available industrial cellulose comes from wood for paper industry and cotton for textile.

In our project, we have focused our attention on the former raw material, because it constitutes the biggest industrial source.

1.2.2 Wood's structure

Trees are the most exploited resource for cellulose due to their wide availability, renewability, and large-scale infrastructure for their converting into several commodities. As the skeletal component in all plants, cellulose is organized in a cellular hierarchical structure. Microfibrils are packed to larger bundles (fibril bundles, fibril agglomerates); hold together thanks to other "matrix" substances like hemicelluloses, lignin and pectin. The wood cell walls (Figure I-7) are divided in several "cell wall layers". The first "cell wall layer" is constituted of middle lamella and primary cell wall layer. The secondary cell wall layer is divided into S1, S2 and S3 with the S2 layer containing the main quantity of cellulose (Core et al. 1979; Fengel and Wegener 1989).

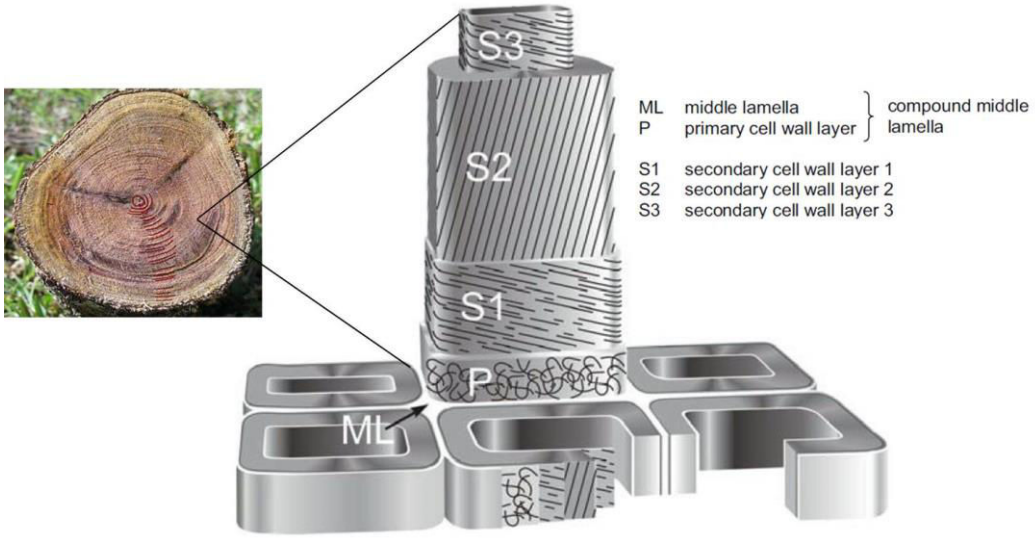


Figure I-7 : Structure of wood (adapted from Eyholzer PhD)

Wood can be defined as a porous, hydrated, and three-dimensional biocomposite composed of an interconnected network of cellulose, hemicelluloses and lignin with dry cellulose content of about 40%. The outermost layer of the cell wall is the middle lamella which is made of lignin and provides adhesion between the layers. The middle lamella is the thin primary wall characterized by a largely random orientation of cellulose microfibrils. In the primary cell wall, hemicelluloses are associated tightly with cellulose fibrils and form a load-bearing network providing mechanical function to the plant (Figure I-8).

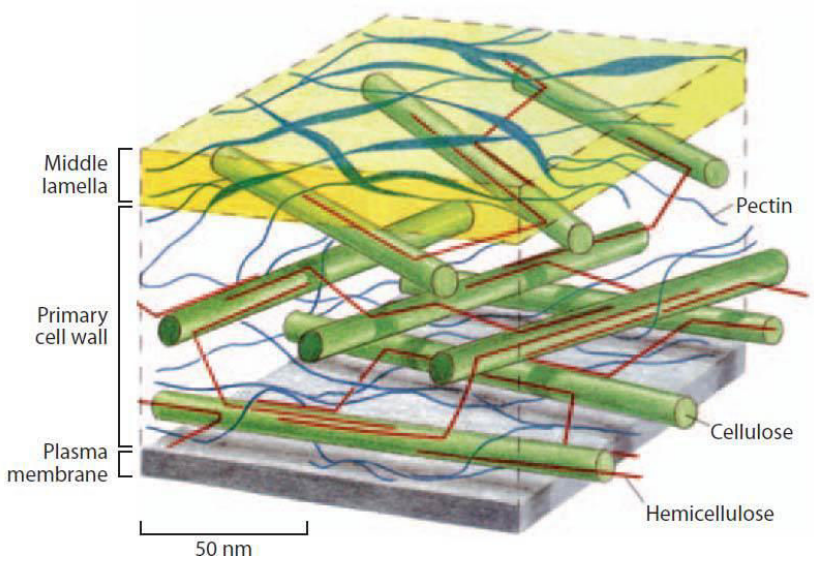


Figure I-8 : Simplified cell wall structure in plant (taken from Rodionova PhD)

The remaining cell wall domain is the secondary cell wall which is composed of three layers: S1, S2 and S3 as already mentioned. S1 and S3 layers are composed mainly of microfibrils glued by lignin and hemicellulose “matrices”. The thick S2 layer, being the richest in cellulose, is arguably the most important in determining the properties of the cell and thus those of the wood at a macroscopic level. The void space in the interior of the cell is called the lumen, which reflects the space available for water conduction.

In wood three main components are present: lignin, hemicelluloses and cellulose. The “matrix” substances in the natural composite of wood are the lignins. **Lignins** are amorphous polymers of aromatic phenylpropane units. In addition to the propane group, the phenyl rings are often substituted with hydroxyl, methoxy, alkoxy or aryloxy groups. In wood, there are typically two main phenylpropane units. Guaiacyl lignin occurs in almost all softwoods and is largely a polymerization product of coniferyl alcohol, containing a hydroxyl and a methoxy group at the phenylpropane unit (Sjöström 1993). Only relatively few phenolic hydroxyl groups are free, most of them are occupied through linkages to neighboring phenylpropane units. In an attempt to illustrate a general structure of lignin, Adler’s formula represents a segment of a lignin macromolecule with some examples of typical phenylpropane units (Figure I-9) (Sjöström 1993).

In our case, all cellulose fibers have been bleached so almost all lignin macromolecules have been removed. Consequently, they will not play any role in our chemical grafting. It is not always the case in literature about NFC (Spence et al. 2010).

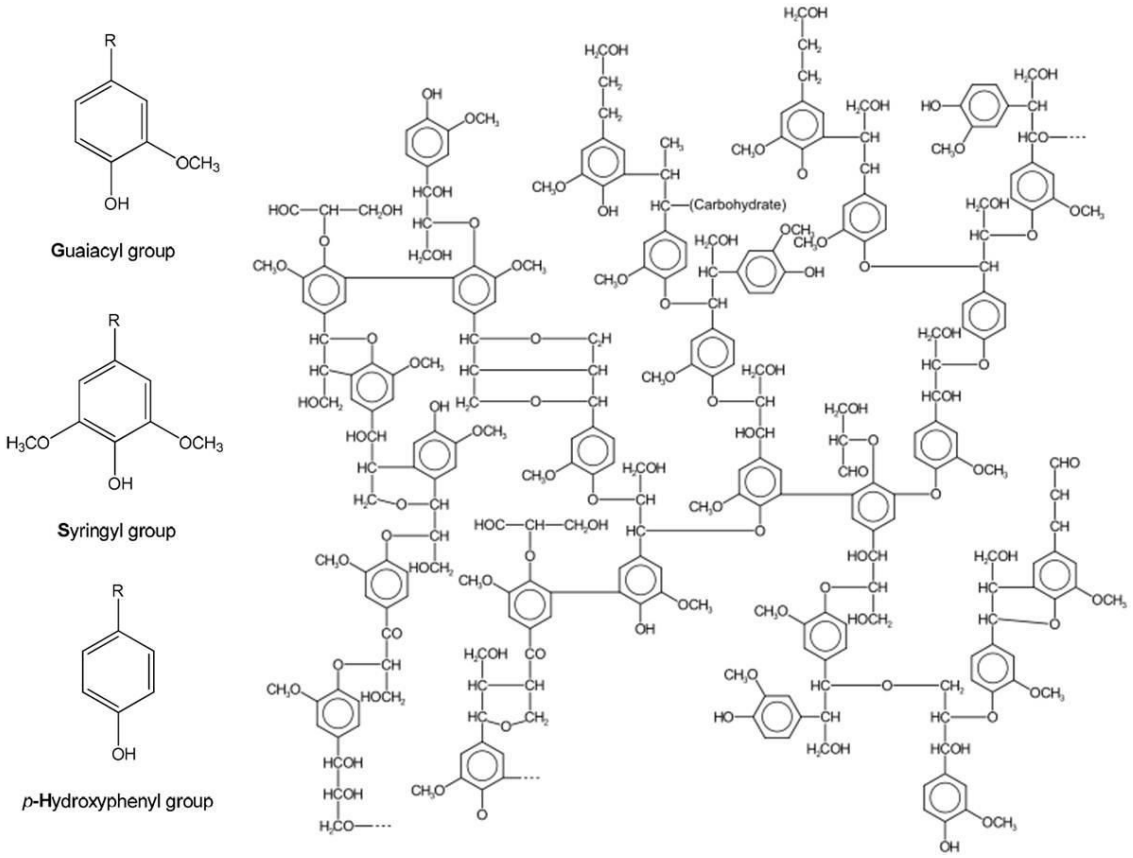


Figure I-9 : Chemical composition of typical lignin according to Adler (taken from Wiki-Lignin web page)

The second component of cellulose fibers is the **hemicelluloses**. The main function of the hemicelluloses is to crosslink the cellulose fibrils with the lignin matrix. The hemicelluloses and celluloses together are often referred as holocellulose. Contrary to cellulose, the hemicelluloses are a family of heteropolysaccharides, with several monomeric components like anhydrohexoses (D-glucose, D-mannose and D-galactose), anhydropentoses (D-xylose and L-arabinose) and Anhydrouronic acids (D-glucuronic acid, D-galacturonic acid). Finally, hemicelluloses can include some acetyl groups in their structures. The quantity and type of each monomer will depend on the type of wood (Tenkanen et al. 2004; Heinze et al. 2006). Most hemicelluloses have a low DP of only 200. Some wood hemicelluloses are extensively branched and are readily soluble in water.

In softwood, the principal hemicelluloses are galactoglucomannans (about 20%). Their backbone consists of a linear chain built up by β (1→4) linked D-glucopyranose and β (1→4) linked D-mannopyranose units (Figure I-10). The α-D-galactopyranose units are linked as a single unit side chain to the framework by (1→6) bonds. The galactoglucomannans can be roughly divided in two groups, one with low galactose content (galactose:glucose:mannose 0.1:1:4), whereas the other contains a higher amount of galactose (1:1:4). In addition to galactoglucomannans, softwoods also contain arabinoglucuronoxylan (about 5-10%). It is

composed of a linear framework of β(1→4) linked D-xylopyranose units. Partially, they are substituted at the C2 by 4-O-methyl-α-D-glucuronic acid groups. In addition, the framework contains also some α-L-arabinofuranose units.

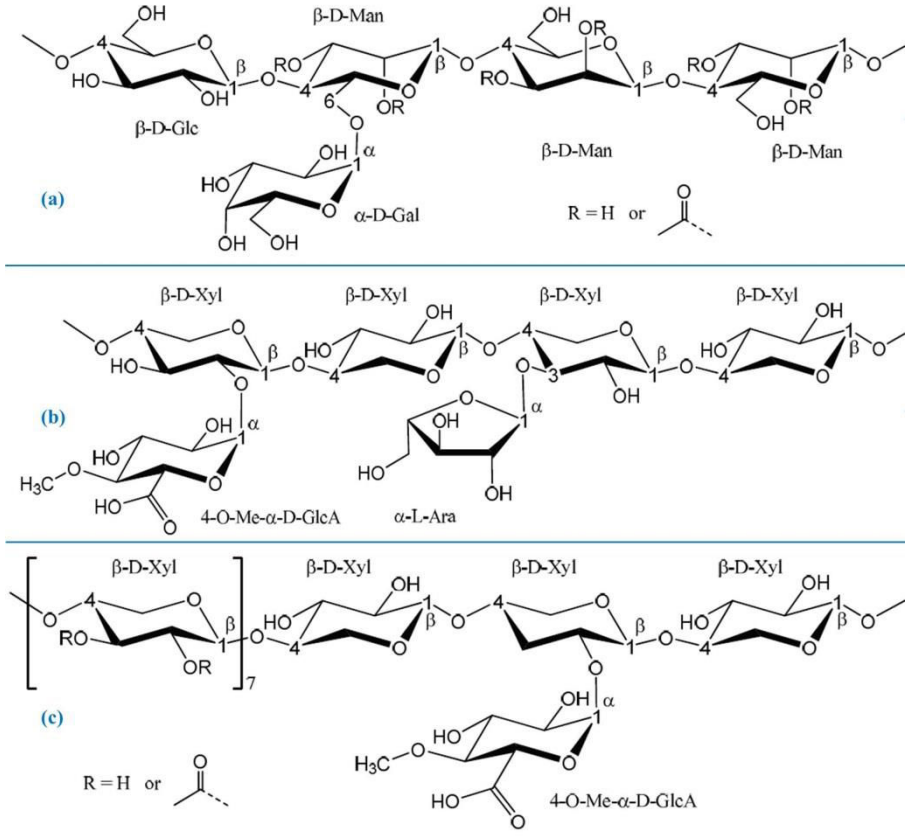


Figure I-10 : Main hemicelluloses present in (a) and (b) softwood and (c) hardwood (Adapted from Eyholzer PhD)

In hardwood, the major hemicellulose component is an O-acetyl-4-O-methylglucurono-β-D-xylan, sometimes called glucuronoxylan. Depending on the hardwood species, the xylan content varies within 15-30% w/w of the dry wood. The backbone consists of β(1→4) linked D-xylopyranose units (Figure I-10). About seven of ten xylose units contain an O-acetyl group at the C2 or C3. In addition, there is on average one (1→2) linked 4-Omethyl-α-D-glucuronic acid residue per ten xylose units. In addition to xylan, hardwoods also contain glucomannan (about 2-5%). It is composed of a linear framework of β(1→4) linked D-glycopyranose and D-mannopyranose units. The ratio between glucose and mannose varies between 1:1 and 1:2. The structure of glucomannan is the same as for galactoglucomannan when omitting the galactopyranose residue. As for the softwoods, there are minor amounts of other polysaccharides present in hardwoods, partly of the same type (Sjöström 1993).

Such components are still present in small amount on cellulose fibers after bleaching treatment. That is why we have to keep in mind their chemical structure when considering surface treatment especially for adsorption processes.

Depending on bleaching process used such hemicelluloses cannot be extracted. Thus, we feel that the description of such operations is necessary.

1.3 Extraction's processes of cellulose fibers

Only cotton can provide quite easily pure cellulose fibers (about 27millions tons produced per year). Usually extraction processes are required and they influence the quality and the chemistry of final cellulose fibers. We can consider different extraction process of cellulose fibers. They depend mainly on two families of the used raw material: (i) the annual plant (Leaf, hemp, jute, kenaf, flax, ramie ….) or (ii) wood and wood-like material.

(i) Annual plant

Even if this raw material has generally low amount of lignin, a drawback of cellulose obtained from higher plants is its chemical impurity, namely the content of residual minerals, especially silica. Pure cellulose can be extracted from the cell wall by using various mechanical, chemical and enzymatic processes. Field retting is a traditional method that consists of discarding the cut fiber stems in the field and leaving the micro-organisms, water, oxygen and UV to aid the release of single fibers from the stems. Carding, also called mechanical decortication, is another common preliminary step aiming at breaking down large fiber aggregates into smaller ones before further treatment is carried out. It has consequences for the fiber integrity such as strain-hardening for example. Progressive reorientation of the microfibrils under stretching is thought to be the mechanism behind this phenomenon (Baley 2002). Thermomechanical pulping, steam explosion, enzymatic retting and mercerization are all four possible treatments that may follow mechanical decortication. They are all aimed at separating the fiber bundles in elementary fibers by extracting amorphous components from the cell wall. Steam explosion consists in placing the wet fibers in a high-pressure environment and suddenly releasing the pressure and temperature down to atmospheric conditions. As a result, fiber bundles break down into single fibers and up to 20% of the fiber mass is removed as hemicellulose and pectin (Baley 2002; Dreyer et al. 2002; Kohler and Nebel 2006). Enzymatic methods are aimed at depolymerizing the hemicellulose and breaking the covalent link between lignin and other carbohydrates (Krässig et al. 2004). Hemicelluloses can also be removed by treatment in hot alkaline solutions followed by neutralization in a mineral acid. When this process is accompanied by fiber stretching, it is commonly referred to as mercerization. *However, all this treatments are archaic (and some ancestral) and concern only a small amount of cellulose fiber (ab. 30 million tons). Nevertheless, they could be of high interest for countries in which such plants are abundant. In our case, we have focused our work on wood pulp, because they are the major source of cellulose fibers in Europe.*

(ii) Wood & woody plant

Pulp consists of cellulose fibers, usually acquired from wood. The liberation of these fibers from the wood matrix can be done mainly in two ways, either mechanically or chemically. Mechanical methods are energy consuming; however they make use of almost the whole wood material and so asses high yield. In chemical pulping, only approximately half of the wood is converted in pulps, the other half is dissolved. However, chemical pulping mills efficiently recover the chemicals and burn the remaining residues. The resulting combustion heat covers the whole energy consumption of the pulp mill (Ek et al. 2009).

The production of pulp for paper was 183 million tons in 2010 (according FAO stats) and 92% of it coming from wood. As represented in Figure I-11, several kinds of pulp can be used for paper production.

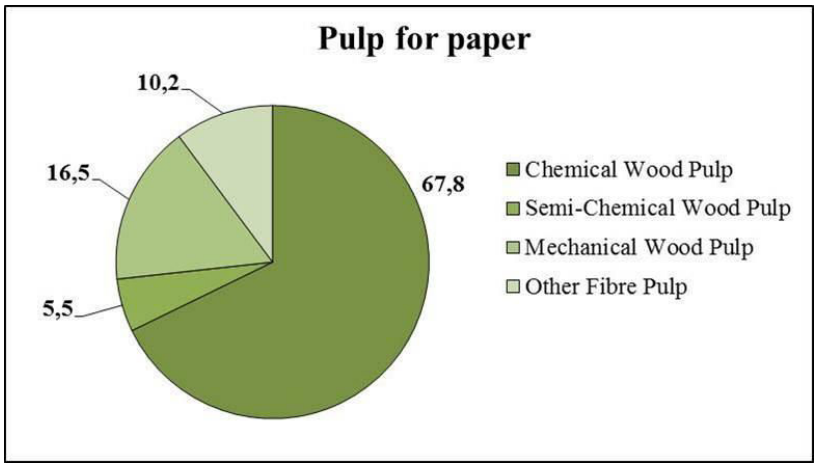


Figure I-11 : World production of pulp coming from different source used for paper application in 2010

The mechanical pulping: Thermomechanical pulping is a common method used to mechanically separate fibers in a liquid media kept at temperatures above 100 °C. Mechanical pulps account for 20% of the world pulp production. Ground wood pulp is produced by pressing round wood chips against a rotating cylinder made of sandstone, scraping the fibers off. Another type of mechanical pulp is refiner pulp, obtained by feeding wood chips into the center of rotating, refining discs in the presence of water spray. The disks are grooved, the closer the wood material gets the edge of the disk, the finer the pulp. Apart from fibers released from the wood matrix, mechanical pulp also contains fines. These are smaller particles, such as broken fibers, giving the mechanical pulp its specific optical characteristics (Ek et al. 2009; Sjöström 1993). The pulp yield is high but there are still lignins and hemicelluloses.

The chemical pulping: The most often applied strategy to isolate cellulose fibers from the wood components is to remove the lignin matrix. Delignification is done by degrading the

lignin molecules, bringing them into solution and removing them by washing. However, there are no chemical reagents being entirely selective towards lignin. Therefore, also a certain amount of the carbohydrates (cellulose and hemicelluloses) is lost in this process. In addition, complete removal of lignin is not possible without severely damaging the carbohydrates structure. After delignification, some lignin is therefore remaining in the pulp and this amount is determined by the pulp's kappa number. Of all pulp produced worldwide (ab. 300 million tons/year), almost three quarters are chemical pulp, of which the major part is produced by Kraft process (Sjöström 1993; Ek et al. 2009).

The kraft process (or sulphate process) is the dominant chemical pulping method worldwide. The cooking chemicals used are sodium hydroxide (NaOH) and sodium sulfide (Na_2S), with OH- and HS- as the active anions in the cooking process. The hydrogen sulfide is the main delignifying agent and the hydroxide keeps the lignin fragments in solution. Optionally, only sodium hydroxide can be used as cooking chemical and this process is called soda cooking (Sjöström 1993; Ek et al. 2009).

The sulfite process involves dissolving lignin with sulfurous acid (H_2SO_3) and hydrogensulfite ions (HSO_3^-) as active anions in the cooking process. More recently developed pulping methods include the use of organic solvents as ethanol, methanol and peracetic acid (CH_3CO_3H) for delignification (Sjöström 1993; Ek et al. 2009). They are called organosolv processes.

As a final step, the pulp can be bleached, to obtain a whiter product with lower amounts of impurities and improved ageing resistance (yellowing and brittleness resistance). These effects are mainly connected to lignin in chemical pulp. Several stages are classically required and different chemicals are used for bleaching, e.g. hydrogen peroxide (H_2O_2), chlorine dioxide (ClO_2), ozone (O_3) or peracetic acid (Sjöström 1993; Ek et al. 2009).

Comparing the *kraft process* and the *sulfite process*, there are numerous differences between the final pulps obtained. Sulfite pulps are more readily bleached and are obtained in higher yields. They are also more readily refined and require less power for refinement. On the other hand, paper from Kraft pulps is generally stronger compared to paper from sulfite pulp, even though the degree of polymerization is lower in Kraft pulp cellulose (Young 1994). Indeed DP usually decreases with pulp treatment and can pass from 14000 to ab. 2500 as mentioned in *section 1.1.1*.

In our study, we have used kraft and sulfite pulps and found that the latter is more suitable for NFC production. We, therefore, focused our effort on sulfite pulps, as a raw material to produce NFC.

1.4 Cellulose Applications

Up today, we consider several areas of application of cellulose fibers (Figure I-12). These elements could be used as such (paper, reinforcing elements, textile...) or after total dissolution (the fiber structure is totally lost), in order to prepare cellulose derivatives and/or regenerated cellulose materials. Table I-1 and give an idea about the different applications. In our case, native cellulose and cellulose derivatives have been uses either as reinforcing elements or matrix in composite, or in papermaking stream. It is also important to note that the highest tonnage is related to paper industry. This industry still grows every year globally and is one of the pioneers for sustainable forest management.

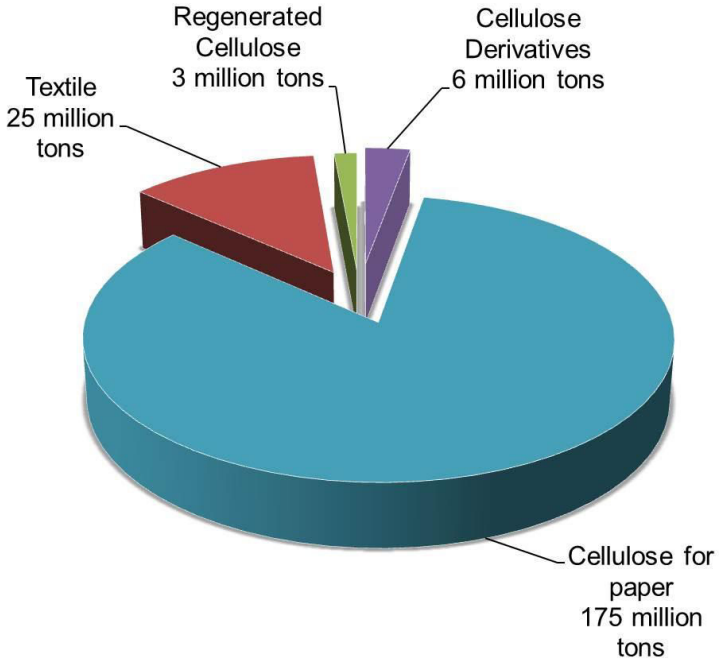


Figure I-12 : Example of cellulose based materials application sector in 2010

Table I-1 : Applications of cellulose in different fields

APPLICATION WITH NATIVE CELLULOSE		
Chemistry	Filtration	Filter paper (acid-hydro cotton linters)
Civil engineering	Concrete reinforcement	Fibers
Commodity	Generic paper, Kraft, cartoon	Paper pulp from hemp, linen, wood,
	Cosmetic use	Cotton wool
	Filtration	Filter paper (acid-hydro cotton linters)
	Hi-fi	Bacterial cellulose audio membranes, loudspeaker or MP3 player composite cases
Electrical	Conductive mats	Cellulose doped with carbon nanotubes
	Transformer insulation	Paper impregnated with insulation oil
Energy production	Heat by direct combustion	Wood
Food	Texturizer, stabilizer and fat replacer	Microcrystalline cellulose
Mechanical	Polymer composites reinforcement	Fibers, whiskers, microcrystals…
	Smart paper	Electroactive paper
Medical	Excipient/drug carriers	Compressed microcrystalline cellulose
Optical	Chiral nematic suspensions of cellulose	Liquid
Textile	Disposable towels, tissues, underwear	Non-woven soft fabrics
	Natural fibers (cotton, hemp, flax…)	Natural fibers
APPLICATION WITH REGENERATED CELLULOSE		
Biochemistry	Ultrafiltration membranes	Membranes
	Fractionation membranes	
	Dialysis membranes	
Biomedical	Artificial blood vessels	Hydrogels
	Cartilage scaffolds	
	Bacterial cellulose wound dressing	
	Wound dressing	Cotton wool
Commodity	Cleaning, liquid absorption	Sponges
	Packaging	Cellophane
Mechanical	Composite matrix	Regenerated cellulose
Optical	Contact lens	Hydrogel
Textile	Man-made fibers (viscose, Lyocel,…)	Regenerated wet-spun cellulose fibers
APPLICATION WITH MODIFIED CELLULOSE		
Chemistry	Purification of chemical systems	Clouding polymers
Civil engineering	Water balance control in building industry materials (concrete)	Cellulose ethers
	Tunneling and slurry supported excavations	Carboxymethyl cellulose
Energy production	Biofuel	Ethanol
	Electricity	Microbial fuel cells to generate electricity by digesting cellulose
Mechanical	Composite matrix	Cellulose derivatives
Paint	Stabilizer	Resin, gels, additives
Textile	Smart textiles	Modified regenerated cellulose fibers

Cellulose is widely used in papermaking industry. Paper is produced from fibrous raw materials such as wood and annual non-wood plants by a process resumed in Figure I-13. The quality of the paper formed depends on the source of the raw material, the refining process used, the additives and aids present in the papermaking formulation and the pressing and drying processes. Converting steps (online and/or offline) can also affect largely the quality of the produced paper.

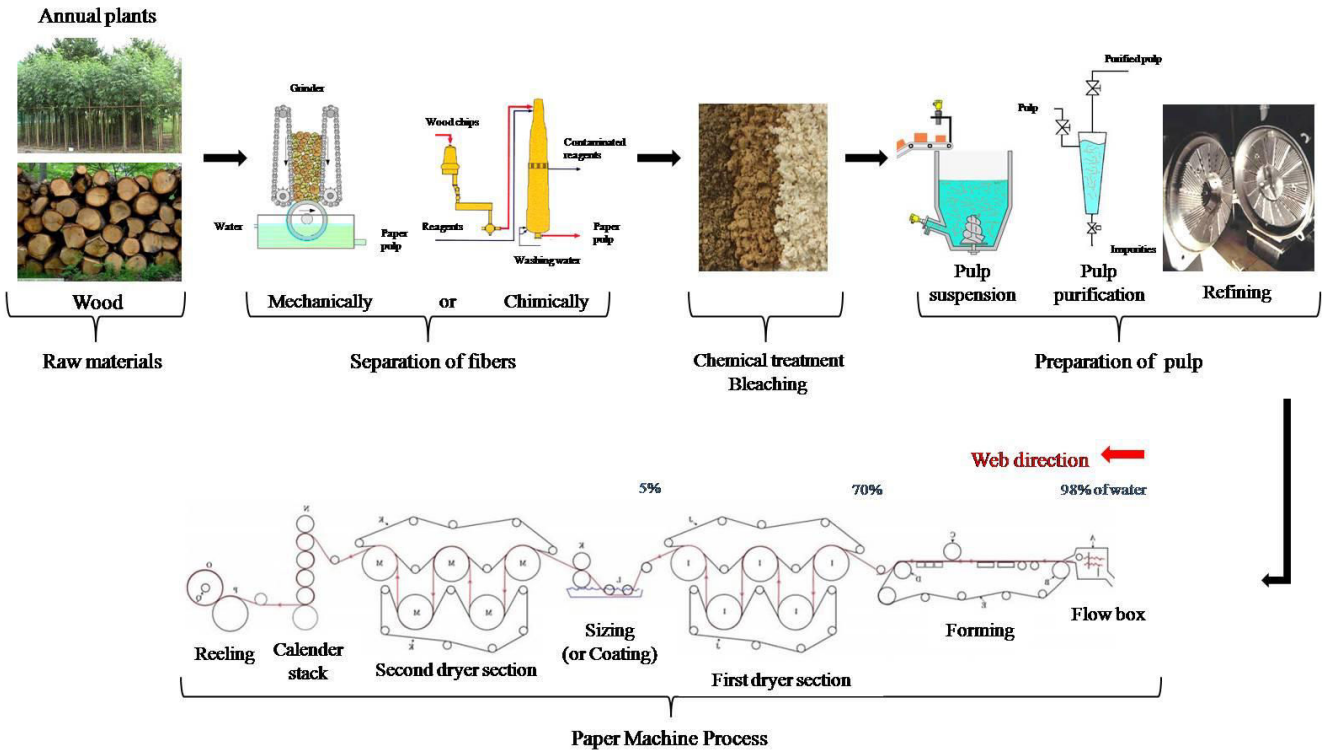


Figure I-13: Schematization of papermaking process (Taken from Denneulin PhD)

The bleached pulp suspension can be purified and refined, before injection on a formation table where the larger amount of water is removed. To eliminate more water and allow hydrogen bond formation (giving the cohesion of the paper), the “wet” web passes through the press section, before entering into a first dryer section. After what, the paper is reeled or sized if needed to impart special properties. A calendaring step can also be applied before reeling to reduce the surface defects and increase the density of the paper.

Paper is well studied material and its main properties are well known. Nowadays, this sector is suffering from a big crisis and two main challenges can boost its economic issues and industrial relevance (i) impart new functionalities to papers without decreasing their properties and (ii) development of new materials based on cellulose destined for other industrial sectors. Chemical modification of cellulose is one of the most promising approaches aiming at providing new functionalities to this raw material. The following chapter will give the state of the art of the different strategies reported in the field.

That's why researchers have focused their work on the development of polysaccharide-based nanoparticles coming (cellulose (NFC or NCC) or starch nanocrystals (Le Corre et al. 2010). Since several decades these bio-based nanoparticles have known a growing interest due to their good properties of reinforcing polymeric matrices or their barrier properties, for example. Several projects were developed and got European financial support for development of these nanoparticles like FlexPackRenew (focused on Starch NanoCrystals) SUSTAINCOMP or SUNPAP projects promoting the development of NFC.

In this report we have worked only with NFC as raw materials. However for a better comprehension of these cellulosic a nanoparticle, the next subchapter is dedicated to NFC and NCC to understand the main difference between these two materials.

2. Chemical modification of cellulosic fibers

Chemical modification of cellulose started more than 100 years ago in order to provide new lignocellulosic functions and to overcome the 2 main drawbacks associated with this raw polymeric material, i.e. the non-solubility and the non-melting ability. Thus, starting from cellulose fibers, two main strategies can be followed: either a “homogeneous” grafting of cellulose, also called derivatization, or a “heterogeneous” grafting of fibers, the so-called surface chemical modification. In fact, the latter keeps the fiber structure of cellulose and concerns only the surface of cellulose fiber.

The idea developed in this context aims at taking benefits from the good performance of the native cellulose fibers, which imposes limiting the modification to the surface. In our study, we have applied this approach to nanofibrillated cellulose, which has roughly the same surface chemistry, but it differs from morphological point of view.

The first strategy (“homogeneous” grafting) consists in solubilizing the cellulose before or during the chemical reaction. A completely different polymer is obtained. Called cellulose derivatives, they can be used in several applications, e.g. foods, cosmetics, plastics, pharmaceutics, coatings etc…

In our study we will use them, in order to prepare nanocomposites, which justify their description (at least briefly) in the following subchapter. The second one will be devoted to detailed description of heterogeneous surface cellulose fiber grafting.

2.1 Cellulose Derivatives: General considerations

Chemical modifications of cellulose generally involve reaction with its hydroxyl groups carried borne by C2, C3 and C6. These –OH reactive groups undergo most of the reactions usually assessed with alcohols. Esterification and etherification of cellulose are the most studied in literature and used in industry.

2.1.1 Cellulose nitrates and esters

In the literature, several esterification reactions are proposed. Inorganic and organic cellulose can be produced. In term of inorganic cellulose, we can found as an example:

(i) Cellulose Nitrate (cf. Figure I-14) is the oldest cellulose derivative (called also Nitrocellulose) and commercially the most important of “inorganic” ester of cellulose. It is well known that applications are in the field of explosives, photography, cosmetics and varnishes.

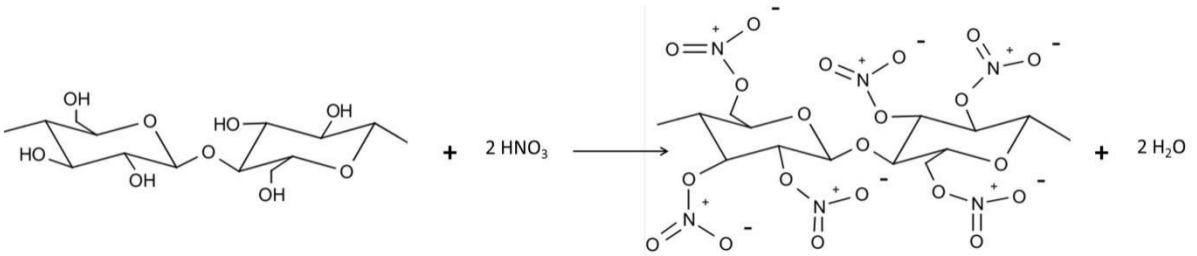


Figure I-14 : Cellulose nitrate reaction

Nitration is usually carried out by treating cellulose with nitric acid in the presence of sulfuric acid and water, as shown in Figure I-14. The amount of water controls the degree of substitution. Table I-3 displays main properties of this cellulose derivative.

(ii) The most important family of organic celluloses esters are obtained by using acyl chlorides or acid anhydrides, as shown for example with cellulose triacetate in Figure I-15.

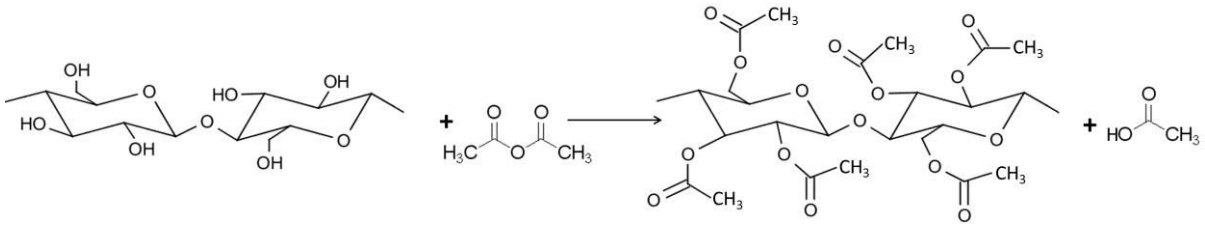


Figure I-15 : Cellulose triacetate preparation using acetic anhydride

Cellulose acetates (CA) are one of the most widely produced cellulose esters. It is an acetylated cellulosic material, in which the hydroxyl groups along the cellulose chain are fully or partially acetylated (Altena and Smolders 1981; Bochek and Kalyuzhnaya 2002; Wang and Fried 1992). Its wide applications in textile fibers, cigarette filters, plastics, films, separation membranes and coating make it the most used cellulose derivatives in industry. All cellulose acetates are generally obtained by reacting high purity cellulose with acetic anhydride, using acetic acid, as reaction solvent and sulfuric acid, as a catalyst. The industrial processes to manufacture a fully substituted cellulose triacetate use, as the solvent medium, glacial acetic acid alone or in combination with methylene chloride as the primary product (DS>2.9, or 92% of hydroxyl group are acetylated). Cellulose triacetate is then isolated and processed as such, or hydrolyzed (by the addition of water, dilute acetic acid or NaOH), in order to “de-substitute” the cellulose triacetate and form secondary cellulose acetate. Thus, a DS between 1.8 and 2.5 can be achieved. These materials are similar to some common plastics and exhibit good mechanical properties, good stability under atmospheric conditions and water resistance (Table I-2). However, melting is almost simultaneous with decomposition. This is the reason why longer grafting moieties or mix of different grafted moieties can be used, in order to introduce internal plasticizer.

Esters of higher aliphatic acids such as cellulose propionate, butyrate or hexanoate are prepared similarly to the acetates derivatives, utilizing either the acid anhydride or the acyl chloride, as the grafting agent. Table I-2 summarizes the different physical and chemical properties of tri-substituted cellulose derivatives.

Table I-2 : Physical properties of cellulose tri-esters grafted with higher carbon number in the aliphatic chains (IDES prospector plastics database)

Number of carbon grafted	Melting point (°C)	Tensile strength (MPa)	Density ($kg.m^{-3}$)	Water sorption (%)
2	306	71.6	1280	2
3	234	48	1230	0.5
4	183	30.4	1170	0.2
5	112	18.6	1130	0.2
6	94	13.7	1100	0.1
10	87	7.5	1030	0.1
12	91	5.9	1000	0.1
14	106	5.9	990	0.1
16	106	4.9	990	0.1

As illustrated in this table, the melting point and the tensile strength of the cellulose esters decrease with increasing length of the ester group. Cellulose butyrate melts without decomposition at 192°C, and therefore can be processed *via* melt state. The cellulose esters with a side chain length containing 3 to 16 carbons can be used to produce increasingly hydrophobic film. But in this case, mechanical properties are also decreased.

Currently, lots of mixed derivatives can be found as Cellulose Acetate Propionate (CAP) or Cellulose Acetate Butyrate (CAB). These mixed derivatives are produced firstly by an acetylation process controlling the DS and then the reaction between the ensuing cellulose acetate and propylic or butyric anhydride is performed. As presented in the Table I-2, cellulose acetate butyrate or propionate can be used as polymeric matrices.

Regarding the large application fields of all these cellulose derivative materials, cellulose acetate derivatives seem to be promising candidates for composite applications. Thus, their mechanical properties, runnability and processability motivate us to produce all cellulose nanocomposites reinforced with NFC and modified, NFC which, to the best of our knowledge, has never been studied in literature. This reinforcement will consist of preparing "all cellulose composites". This point will be investigated in the last chapter of the present report.

2.1.2 Cellulose ethers

Cellulose ethers are a wide range of cellulose derivatives such as carbomethylcellulose (CMC), methyl cellulose (MC), hydroxyethyl cellulose (HEC) hydroxypropylcellulose (HPC), hydroxyethylmethylcellulose (HEMC) and hydroxypropylmethylcellulose (HPMC). Their main property is their solubility in aqueous solutions. They are used, as additives in various industries including food, paint, oil, paper, cosmetics, adhesives, printing, textile… Cellulose ethers act as thickeners water retention agents, film former or thermoplastics in these applications.

(i) Alkyl ethers of cellulose, as methylcellulose or ethylcellulose are obtained following the process detailed in Figure I-16.

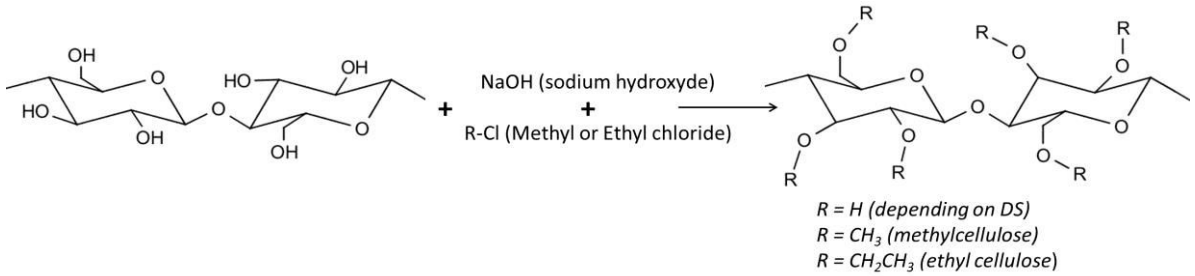


Figure I-16 : Chemical reaction to obtain methyl or ethyl cellulose derivatives

It results from a nucleophilic attack of the alkoxide group of cellulose on the acceptor carbon of methyl or ethyl chloride. It requires high temperature and high amount of NaOH (40%) in comparison to the viscose process which, instead, requires only 18%. Reactions are occurred preferentially at the C2 and C6 hydroxyl sites. Hydrophobicity of alkylcelluloses increases with the length of the alkyl chain and with the DS of the derivative (cf. Table I-3).

(ii) Carboxymethylcellulose or CMC is a water-soluble anionic polymer achieved by introducing carboxymethyl groups along the cellulose chain (Figure I-17). CMC is usually synthesized by the alkali-catalyzed reaction of cellulose with chloroacetic acid (Heinze and Koschella 2005). The functional properties of CMC depend on the degree of substitution of the cellulose structure and on the chain length of the cellulose backbone.

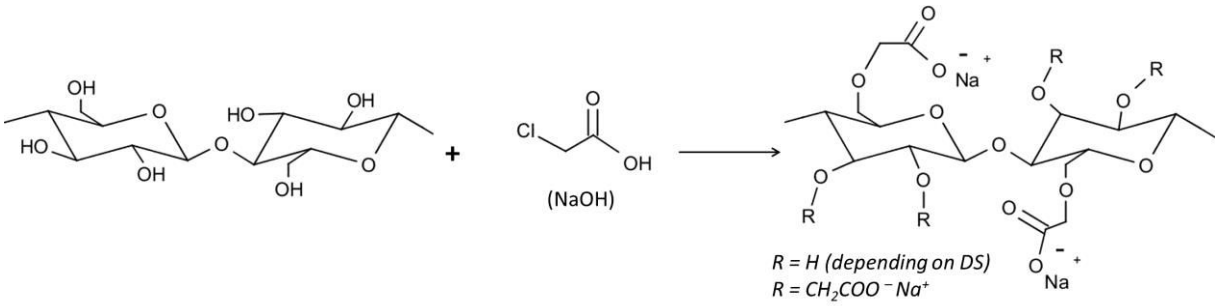


Figure I-17 : Chemical reaction for preparation of carboxymethylcellulose

The degree of substitution (DS) of CMC is usually in the range of 0.6 to 0.95 derived groups per monomer unit. CMC is generally considered as a water-soluble polymer down to DS 0.3 (Fox et al. 2011; Horsey 1947). CMC displays interesting properties, as shown in Table I-3. Aqueous solution of CMC acts as thickener, rheology control agent, binder, stabilizer, film former and water retention aid. Thus, it can be employed in various industries as cosmetic, pharmaceutical, food, paper, adhesives, coatings… Such a material has similar chemistry as TEMPO oxidized NFC (detailed previously), which justify a brief discussion of CMC family. In fact, our studies on TEMPO oxidized NFC (NFC-TE) will take advantage from such an insight. Nevertheless, the main difference is that CMC is in aqueous solution, whereas NFC-TE particles are in water suspension. In this case we will speak about heterogeneous grafting.

Table I-3: Some physical properties of carboxymetylcellulose (Wertz et al. 2011)

Properties	Nitro cellulose	Tri acetate	2nd acetate	CAB (DS=3.2)	CAP (DS=3)	Methyl cellulose	Ethyl cellulose	Carboxy methyl cellulose
Mechanical Properties								
Tensile strength(MPa)	35-70	137-245	157-177	24-76	/	10-12	42-62	55-105
Elongation (%)	10-40	20-35	2-16	8-80	/	7-14	0.1-0.4	8-14
Physical Properties								
Melting point (°C)	145-152	> 260	230	115-165	185-230	290-305	240-255	/
Glass temp. (°C)	70-80	/	/	56-94	115-145	140-165	80-130	-40-70
Density ($kg.m^{-3}$)	1.3-1.4	1.27-1.29	1.28-1.32	1.15-1.22	1.28-1.32	1.01-1.10	1.07-1.18	1.59
Water sorption	0.6-2	2.5-3.2	2-10	/	/	Soluble	1-3	Soluble

2.2 Heterogeneous grafting in solvent media

Several reactions dealing with the surface chemical grafting of cellulose fibers can be found in the literature. Various authors have reviewed research related to this field, especially those by which macroscopic cellulosic fibers can be rendered less hydrophilic and more compatible with hydrophobic matrices (Belgacem and Gandini 2005; Bledzki et al. 1998; Eichhorn et al. 2001; Jacob et al. 2005; Lindström and Wagberg 2002; Lu et al. 2000; Mohanty et al. 2001; Trejo-O'Reilly et al. 1997).

In this report we are focused our attention on only 2 types of modification i.e. carbanilation using isocyanate and esterification of cellulose using anhydride moieties (aliphatic anhydride and Alkyl Ketone Dimer (AKD) reaction). That is why, in the next chapter, only these two reactions will be studied.

However research on sylilation (Belgacem and Gandini 2011), etherification and many others are available in the literature, as recently review by Gandini and Belgacem (Gandini and Belgacem 2011)

The following chapter deals with chemical grafting and will be divided into two main sections. The first one will cover grafting with small molecules, whereas the second will be devoted the polymer-assisted grafting.

2.2.1 Molecule chemical grafting

Isocyanates or **di-isocyanates** are known in polymer chemistry (e.g. polyurethane) but also in wood chemistry, as wood binders with successful applications. The -N=C=0 group of isocyanate is highly reactive with the -OH group of cellulose and it yields urethane linkage. Extensive experimental work on the application of isocyanate, as coupling agents for different types of cellulose materials and polymers, has been carried out by Kokta and co-workers (Kokta et al. 1990). Composites were manufactured with cellulosic material, which was either pre-coated with an isocyanate polymer mixture, or the isocyanate was added directly into the mixture of the fibers and the polymers. Thomas' group (George et al. 1997; Joseph et al. 1996) also reported on the mechanical properties of isocyanate treated fiber reinforced thermoplastics composites. Sisal fibers were treated by urethane derivatives of cardanol and found that such a treatment improves the compatibility between fiber and matrix. The poly(methylene1 poly(pheny1) isocyanate (PMPPIC) treatment has significant influence on the properties of the composites, i.e., increased thermal stability, reduced water absorption and mechanical properties (George et al. 1996; Mishra et al. 2004). PMPPIC is chemically linked to the cellulose matrix through strong covalent bonds. More recently, Krouit

et al. (Krouit et al. 2010) compared these chemically grafted fibers with extracted fibers for compatibilizing in biocomposites and proved the beneficial effect of such a treatment. Ly et al. (Ly et al. 2008) and Bessadok et al. (Bessadok et al. 2010) also demonstrated the positive impact of using di-isocyanate regarding mechanical properties of biocomposite. Joly et al. (Joly et al. 1996a) studied the effect of alkyl isocyanate treatment on the water absorption behavior of cotton cellulose-reinforced composites by varying the length of alkyl chains. Their results showed the importance of critical length of the alkyl chain for reducing the amount of adsorbed water when working with isocyanate. It is worth to notice that, in the presence of traces of humidity, isocyanates will react preferably with water instead of hydroxyl group of cellulose to produce amine ($R\text{-}NH_2$). The ensued amine could react with other isocyanate and to form di-substituted urea, which can be considered as by-products, as schemed in Figure I-18.

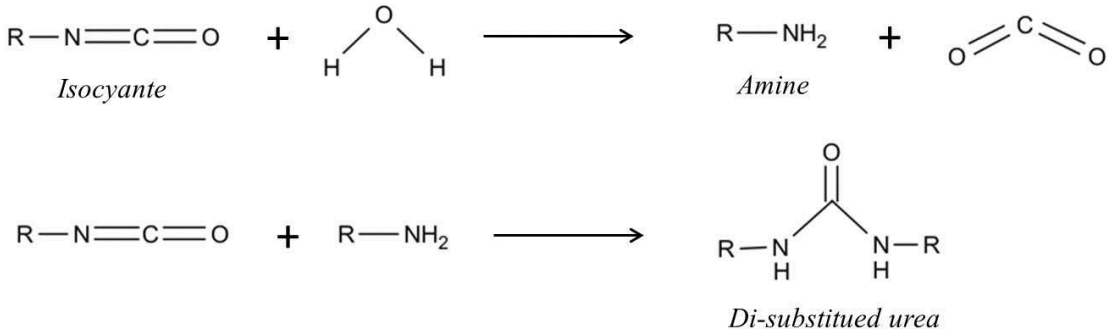


Figure I-18 : Secondary reaction occurred with isocyanate

Because of their basic character, these moieties can further react with isocyanates, yielding side chains called allophanate. Rensch and Reidl (Rensch and Riedl 1992) modified chemo-thermo-mechanical-pulp (CTMP) with various isocyanates such as n-butyl isocyanate (BUI), phenyl isocyanate (PHI), hexamethylene di-isocyanate (HMDI) and poly(methylene) poly(pheny) isocyanate (PMPPIC) in DMF, in the absence of catalyst. The effect of such a treatment on the thermoanalytical behavior of CTMP was investigated. Aliphatic isocyanates such as BUI and HMDI showed a low potential of reaction with CTMP, compared to MDI and PHI. The use of MDI and its oligomeric homologues PMPPIC, as coupling agent, resulted in an increased thermal stability of modified pulp when compared to untreated counterpart.

The **esterification** of cellulose is very old reaction which first applied to the synthesis of cellulose acetate, as described previously. This reaction can be limited to the surface of cellulose fibers, by using non-swelling solvents. The most extensively explored reagents are acetic anhydride, alkyl ketene dimer (AKD), alkenyl succinic anhydride (ASA) and different fatty acids (with carbon number of the aliphatic chain varying from 6 to 22) or their chlorides. Ester formation is a popular way to impart hydrophobic nature of cellulosic surfaces (Alvarez

et al. 2007; Belgacem and Gandini 2009; Caulfield et al. 1993; Felix and Gatenholm 1991; Gandini and Belgacem 2011; Joly et al. 1996b; Matsumura and Glasser 2000; Pasquini et al. 2008; Pasquini et al. 2006; Zafeiropoulos et al. 2002a; Zafeiropoulos et al. 2002b). As proposed by Freire et al. (Freire et al. 2005), in specific conditions (non-swelling solvent), cellulose fibers can be modified at their surface with several fatty acyl chlorides (hexanoic C_6, dodecanoic C_{12}, octadecanoic C_{18} and docosanoic C_{22}). As shown in the Table I-4, several times of reaction and solvents were applied.

Table I-4 : Surface chemical modification of cellulose fibers by esterification (adapted from Freire et al. 2005)

Fatty acid chloride	Solvent	Reaction time	DS
Hexanoic	Toluene	0.5	0.43
		1	0.51
		2	0.85
		4	0.80
		6	0.75
		6	***1.06***
Dodecanoic		0.5	0.18
		1	0.40
		2	0.73
		4	1.13
		6	1.43
		6	***1.37***
Octadecanoic	***DMF***	0.5	/
		1	/
		2	0.076
		4	0.12
		6	0.30
		6	***0.94***
Docosanoic		0.5	/
		1	/
		4	0.022
		6	0.067
		6	***1.22***

In this paper, authors used TGA and contact angle measurements to demonstrate that materials with increased thermal resistance and hydrophobic character could be obtained.. Depending on the solvent used, cellulose fibers seem to be more reactive in DMF. However the crystallinity index is strongly reduced for lower aliphatic fatty chlorides (i.e. C6 and C12) even if the fiber structure is conserved. We can suppose that reactions have been performed at the surface of fiber but also in depth of the materials.

In our study different length of anhydride will be investigated and compared from C2 to C6. (See Chapter 2.2)

In 2007, Cunha et al. published three papers dealing with the surface esterification of cellulose fibers with different perfluorinated reagents, viz. trifluoroacetic anhydride (TFA) (Cunha et al. 2007c), pentafluorobenzoyl chloride, PFB (Cunha et al. 2007a), and 3,3,3-trifluoropropanoyl chloride, (TFP) (Cunha et al. 2007b), under controlled heterogeneous conditions. The occurrence of the grafting was demonstrated by direct techniques, such as FTIR, XPS and ToF-SIMS, whereas the hydrophobic and lipophobic character of the fluorine-containing modified surfaces were found to increase significantly compared with those of the pristine fibers. The degree of substitution of the pentafluorobenzoylated substrate ranged from 0.014 to 0.39, whereas that of the trifluoropropanoylated counterpart ranged from less than 0.006 to 0.30. The thermal stability decreased only slightly following this treatment, whereas the degree of crystallinity decreased significantly under the most severe experimental conditions.

This esterification of cellulose surface can also occur with di-anhydride as coupling agent in biocomposite. Positive effect on mechanical properties has been achieved by Ly et al. (Ly et al. 2008). The main problem with such molecule grafting is the need:

(i) of non-aqueous solvent to avoid the secondary reaction or deactivation of reagents; and

(ii) of non-swelling solvent to limit the occurrence of the reactions inside the fiber cell wall, thus avoiding the destruction of the fibers and the loss of their physical and mechanical properties.

2.2.1 Polymer grafting

Several strategies can be detailed for grafting cellulose by polymeric architectures: (i) the use of mono-activated polymer (“grafting onto”) or (ii) *in-situ* polymerization of monomer starting from an active site of the solid under investigation (“grafting from”). The latter one has similar issues, as those associated with small molecules grafting and can occur into homopolymer. Such strategy will be presented more in details when discussing NFC grafting (Chapter 1.3) and at the end of this subsection with specific polymerization mechanisms.

Concerning the first strategy, it was recently showed that cellulose fibers can be successfully modified with functionalized activated polymer or oligomer. Ly et al. (Ly et al. 2010) activated poly(ethylene), poly(propylene) and poly(tetrahydrofuran) glycols by converting them mono-NCO-terminating macromolecules. The ensuing mono-activated polymer has reacted with cellulose fibers in DMF and the resulting fibers have been analyzed by SEM as shown in Figure I-19. These macromolecules were coupled with cellulose surface and then characterized using FTIR, contact angle and XPS measurements.

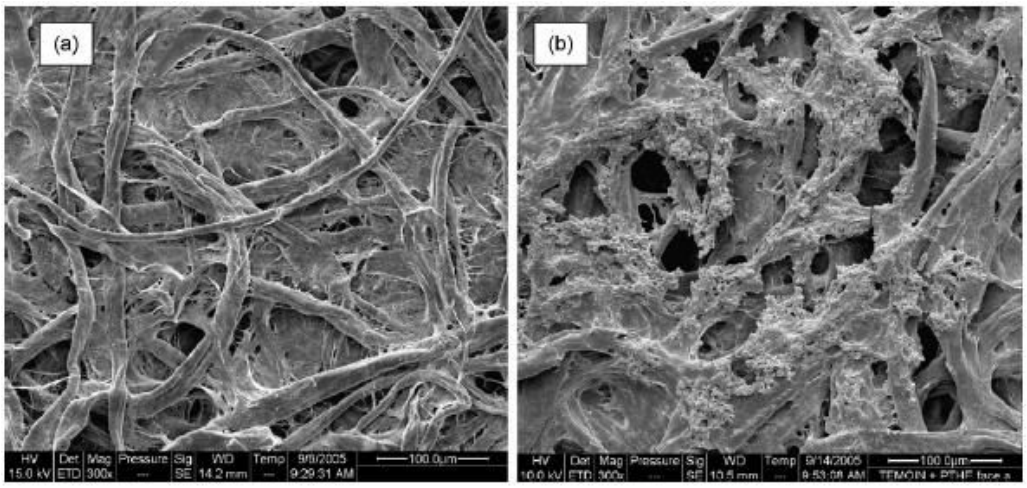


Figure I-19 : SEM observation of (a) non grafted and (b) grafted whatman fibers with Poly(Propylene)Glycol (Ly et al. 2010)

Others characterizations showed clear cut evidences about the occurrence of grafting (i.e. surface energy decrease, water contact angle stiffed from 40° to 90°, detection of nitrogen signal by elemental analysis and XPS measurements). The same idea has been successfully achieved by using poly-caprolactone (PCL), as grafted polymer (Paquet et al. 2010). The XPS deconvolution of C1s signal show clearly the occurrence of grafting.

Other technique using “click chemistry” was developed in heterogeneous conditions (Hafrén et al. 2006; Vogt and Sumerlin 2006; Zhao et al. 2010). Krouit et al. (Krouit et al. 2008) grafted successfully using this method PCL onto cellulosic fibers following three steps, as presented in Figure I-20.

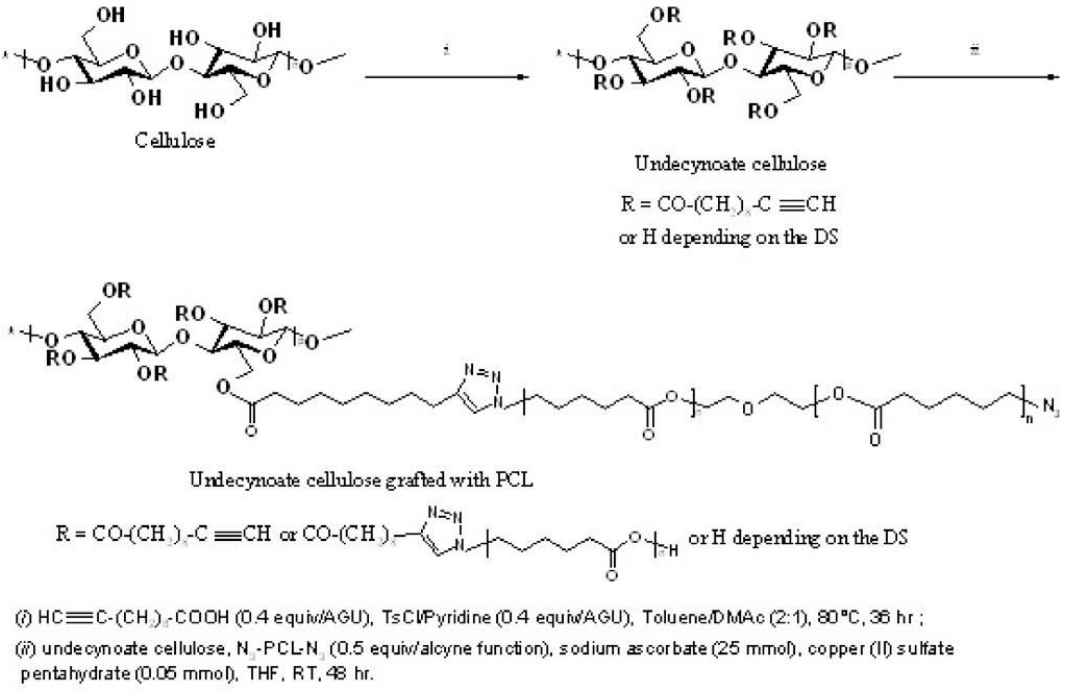


Figure I-20 : Strategy of cellulose surface modification by click chemistry (Krouit et al. 2008)

In this work, the first step consisted of the esterification of cellulose in a mixture toluene/DMAc in order to use non-swelling solvent conditions. XPS characterizations showed the grafting thank to deconvolution of C1s signal. The second step was to convert PCL-diol into azido-PCL. Last step was dedicated to the “click” reaction between azido-PCL and cellulose ester was monitored by FTIR spectroscopy. XPS data showed clearly the grafting and the successful reaction between PCL and cellulose.

Concerning the second strategy, i.e. “grafting from”, cellulose fibers were grafted with poly(styrene) by RAFT (Reversible Addition-Fragmentation chain Transfer) polymerization (Roy et al. 2005) and the ensuing materials were thoroughly characterized to prove the occurrence of the desired modification, which reached high yield of polymerization. The results suggest that the hydrophobic character of the grafted copolymers increased with increasing percentage of the grafting (from 11% to 26%). Static contact angle values for all the grafted copolymers were found to be around 130° with water.

ATRP (Atom Transfer Radical Polymerization) grafting from cellulose has been the subject of several investigations aimed at preparing liquid crystalline grafts (Carlmark and Malmström 2002; Westlund et al. 2007) and thermo- and pH-sensitive materials (Ifuku and Kadla 2008; Lindqvist et al. 2008). Recently, cellulose was also grafted with various monomers using activators regenerated by electron transfer (ARGET), a version of ATRP (Hansson et al. 2009). Cellulose membranes were modified using surface-initiated polymerization (ATRP) for blood compatibility improvement (Liu et al. 2009) calling upon a two-step process consisting of grafting, first, 2-bromoisobutyl bromide and then polymerizing *p*-vinylbenzyl sulfobetaine (DMVSA) from it. The modified cellulose membrane substrates were characterized by FTIR, XPS, water contact angle measurements, AFM and TGA, which showed that the grafted brushes had been successfully appended onto the cellulose membrane surfaces, and that their density had increased gradually with increasing polymerization time.

So, as presented before there are several methods to chemically modify cellulose fibers. But in our work we are focused only on green process which involved less solvents or water-based reaction media. This objective will be investigated in the next section.

2.3 "Green" processes for modification

2.3.1 Without solvent

An interesting and environmentally surface treatment concerns the use of atmospheric air pressure **plasma** (AAPP), which was recently applied to various lignocellulosic fibers (abaca, flax, hemp and sisal) limited to a few minutes to render fibers more hydrophobic. Plasma treatment has been used for a while in textile industry but barely in paper and composite. The wettability of the treated fibers surface (Baltazar-y-Jimenez et al. 2008) was determined using the capillary rise technique, whereas the changes in the surface chemistry were characterized by zeta-potential measurements. The surface energy of the lignocellulosic fibers was found to remain practically constant, even for prolonged treatment times, with the exception of the abaca fibers, for which this parameter decreased with increasing AAPP treatment time. Recently, Gaiolas et al. published two papers dealing with the treatment of cellulose samples with cold plasma in the presence of several coupling agents, namely vinyl trimethoxysilane, g-methacrylopropyl trimethoxysilane, (Gaiolas et al. 2008), myrcene and limonene (Gaiolas et al. 2009). The modified substrate was extracted, in order to remove the physically adsorbed unbound molecular moieties, before being characterized. Contact angle measurements and XPS showed that the surface cellulose chains had indeed been chemically grafted, as indicated by an increase in the water contact angle from 40° to more than 100° and the corresponding decrease of the polar component to the surface energy from about 23mJ.m^{-2}, to almost zero, for all the treated samples. Other authors developed several methods using plasma discharge to modify cellulosic substrates. A superhydrophobic cellulose surface was reported (Balu et al. 2009), as a result of a double plasma treatment. Contact angles as high as 167º were attained under optimized conditions. Vesel et al. (Vesel et al. 2009) treated viscose textiles with oxygen, nitrogen or hydrogen plasmas for 5 s.

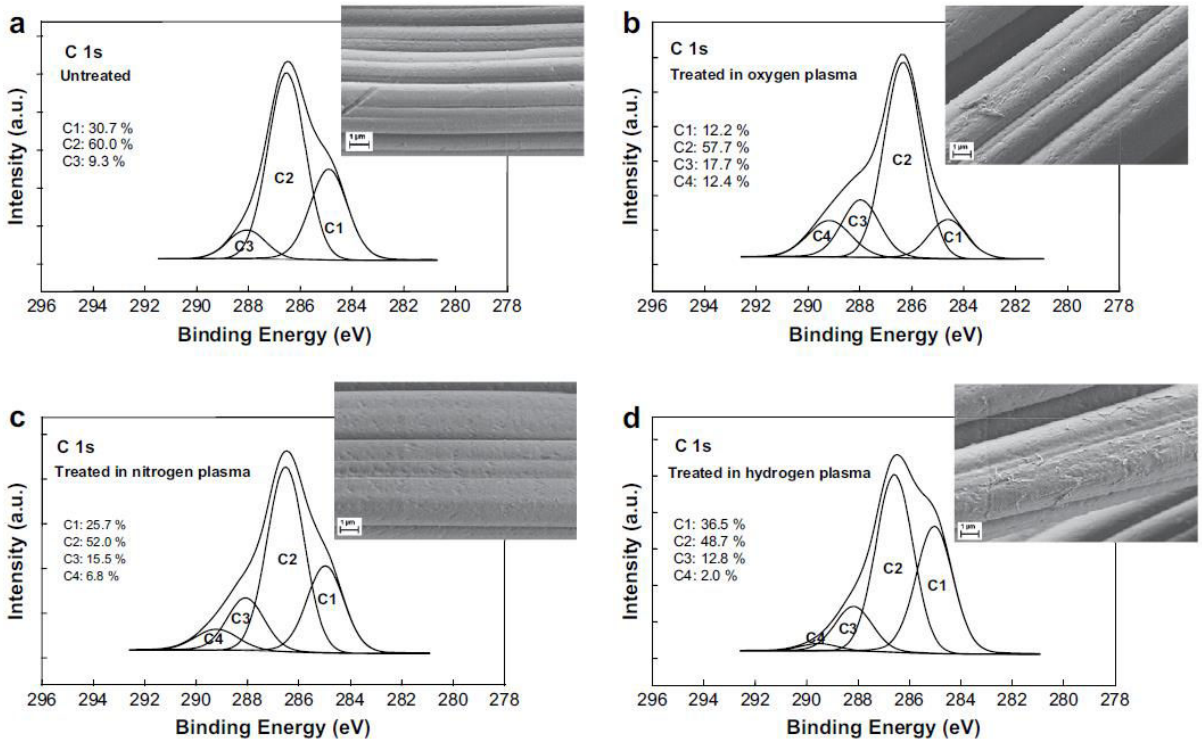


Figure I-21 : SEM images and C1s high-resolution of viscose textile (a) untreated, and after 5s with (b) oxygen plasma, (c) nitrogen plasma and (d) hydrogen plasma (adapted from Vesel et al. 2009)

High-resolution XPS (Figure I-21) showed that the use of oxygen and nitrogen atmospheres induced a strong oxidation of the surface, whereas hydrogen, as expected, caused a substantial decrease in oxidized moieties. Moreover, plasma treatment under a stream of nitrogen caused the fixation of N atoms, as detected by XPS. SEM images showed an increase in the fiber surface roughness after treatment with hydrogen or oxygen plasma.

Other possibility for grafting cellulose without any solvent is to use volatile reagent molecule. Recently, Belgacem's group (Cunha et al. 2010) managed grafting volatile silanes onto Whatman paper by using gas-solid reaction of reagent located in the other side of the sample to be grafted. In this case, water vapor was added to achieve silane grafting. Results were promising and similar strategy have been used for nanocellulose (Berlioz et al. 2009; Rodionova et al. 2010) and will be detailed in next subchapter.

It is also possible to add directly the reagent onto paper and to activate reaction by increasing the temperature. This solution is well known for acyl chloride since the 90's and some researchers called it chromatogeny (Samain 2002). Indeed the reagent is coated on the substrate surface and the reaction proceeds by its evaporation and elution through the sample thickness thank to a stream of a vector gas. Very recently, the "Centre Technique du Papier" (CTP) in France build a pilot roll-to-roll on this strategy with very promising first samples. To the best of our knowledge, such an approach has never been used for nanocellulose grafting.

2.3.1 Ionic liquids as green solvent

Ionic liquids or “molten salts” are in general defined as liquid electrolytes composed entirely of ions. Recently, the melting point criterion has been proposed to distinguish molten salts (“high melting point, high viscosity and corrosive medium”) and Ionic Liquids (“liquid below 100°C and lower viscosity”) (Baker et al. 2005; Hardacre 2007; Holbrey and Seddon 1999). The most important features of ILs are their non-measurable vapor pressure. Indeed, they are defined as “green” solvents mainly because they are non-volatile organic compounds (VOC). In addition to this property, ILs have other attractive properties such as chemical and thermal stability (Blake et al. 2006; Chiappe and Pieraccini 2005; Zhang et al. 2006), non-toxicity for humans regarding inhalation, non-flammability and high ionic conductivity which constitute interesting parameters for chemical modification. They could be also easily recyclable and reused due to their low melting point (comprising -60°C to 60°C) just by solidification decreasing the temperature or by distillation (e.g. evaporation of by-products). For these reasons, ILs are very promising for replacement of traditional volatile organic solvents. There is a wide variety of ILs, each of them are composed of a cation, mainly two type imidazolium or pyridinium salts, and an anion (e.g. chloride, tetrafluoroborate, hexafluorophosphate…), as presented in Figure I-22.

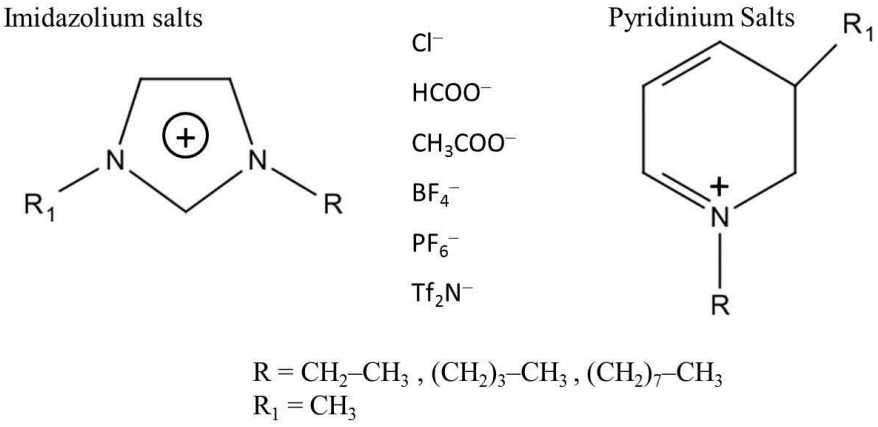


Figure I-22 : Different type of Ionic liquids

The decomposition temperatures reported in the literature are generally superior to 400°C, with minimal vapor pressure below their decomposition temperature (De Azevedo and Esperanca 2005a; De Azevedo and Esperanca 2005b; Cropsthwaie and Fredlake 2004). ILs are denser than water and arise high viscosity (Tomida et al. 2006) which can reduce the diffusion rate of reagent molecules for chemical reaction. The Table I-5 represents different ILs and their properties.

Table I-5 : Ionic liquids properties

IL abbreviation	Molecular weight ($g.mol^{-1}$)	Melting point (°C)	Viscosity (mPa.s)	Solubility in water
[bmim][Cl]	174,67	~ 60	Solid	C.S*
[emim][BF_4]	197,97	~ 15	~ 37-66	C.S*
[bmim][BF_4]	226,02	~ -70	~ 132-233	C.S*
[omim][BF_4]	282,13	/	~ 325-400	9,14 %wt.
[emim][PF_6]	256,13	~ 59	/	5,09 %wt.
[bmim][PF_6]	**284,18**	**~ 12**	**~ 385-450**	**2,12 %wt.**
[omim][PF_6]	340,29	~ -71	~ 682-847	0,95 %wt.
[emim][Tf_2N]	391,32	~ -16	~ 28-39	1,37 %wt.
[bmim][Tf_2N]	419,37	~ -3	~ 52-69	1,10 %wt.
[omim][Tf_2N]	447,42	/	~ 80-93	0,75 %wt.

The chemistry and the interactions between cellulose and ionic liquids have been investigated during the ten past years, but mainly for solubilization or homogeneous derivatization of cellulose (Biswas et al. 2006; Feng and Chen 2008; Swatloski et al. 2002). Ionic liquids are promising solvent for homogeneous chemical reaction on cellulose, but they have also the capacity to degrade cellulose fibers (Heinze et al. 2008). To limit this phenomenon, a hydrophobic IL could be used and different parameters must be considered (i.e. viscosity, polarity, affinity with water, dissolution in water) (Freire et al. 2007; Rivera-Rubero and Baldelli 2004; Shvedene et al. 2005; Wong et al. 2002). For instance, Liebert and Heinze (Liebert and Heinze 2008) reviewed several methods using IL for the esterification of cellulose fibers in homogeneous cellulose. Figure I-23 displayed some derivatives obtained after homogeneous chemical reaction.

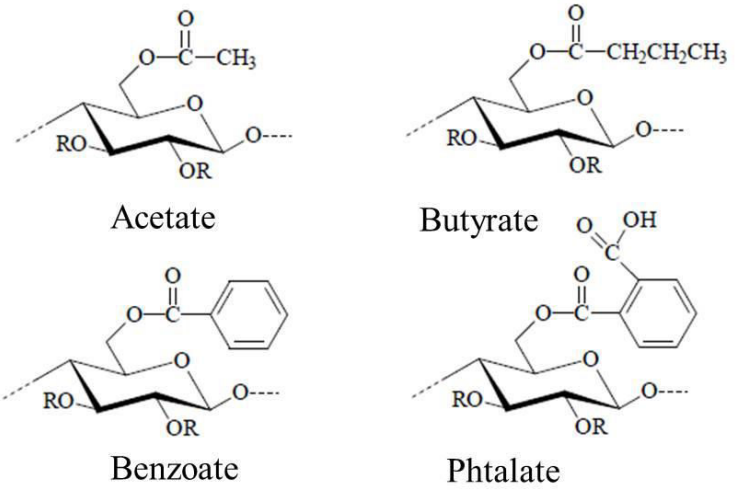


Figure I-23 : Cellulose tri-esters prepared in the solvent N-benzylpyridinium chloride/pyridine (Liebert and Heinze 2008)

The DS obtained was close to 3 for all the samples for 2 hours of reaction. Among a large variety of ILs, only few of them are immiscible with water and could perform heterogeneous media surface modification of cellulose. To our knowledge nobody has already grafted cellulose fiber surface by heterogeneous reaction within ionic liquid in spite of the promising "green" properties of these solvents. The hydrophilic / hydrophobic balance is important for the solvatation properties of ILs but it is also relevant for the recovery of products by solvent extraction for example.

Several procedures have been developed to recycle ILs with an acceptable degree of purity. Liquid-liquid extraction or cooling has been used to remove impurities (Chapeaux et al. 2008; Dupont et al. 2002; Earle and Seddon 2000; Muthusamy and Gnanaprakasam 2005; Zhao et al. 2005). After heterogeneous reaction, modified materials could be easily removed by filtration and the impurities, by-products and unreacted moieties can be removed by liquid extraction or distillation.

In Chapter 2, the chemical surface modification of nanofibrillated cellulose in ionic liquids will be investigated in heterogeneous conditions for the first time in literature.

2.3.2 Water-based modifications

(i) Silanation in water is a silane-based reaction, which can be used to attach a wide range of functional groups on the surface of cellulose fibers. Numerous studies have dealt with the modification of cellulosic materials with silanes to improve their performance when used in composite (Abdelmouleh et al. 2007; Abdelmouleh et al. 2005; Bledzki and Gassan 1999; Gassan et al. 2000; Matuana et al. 1999; Pothan et al. 2007; Singh et al. 1996). The mechanism of silanation coupling reaction has been described by Castellano et al. (Castellano et al. 2004). In the strict absence of water, SiOR groups apparently do not react

with cellulosic hydroxyl groups. Thus, moisture and water can lead to partial hydrolysis of the silane rendering it reactive with hydroxyl groups of cellulose fibers by deshydratation when the samples are dried. The fundamental mechanisms of this reaction have been detailed very recently (Paquet et al. 2012). It is one of the main reactions in aqueous media. Other possibilities are (i) either grafting oxidized cellulose with alcohol or amine for example or (ii) working with emulsions.

(ii) Indeed, the AKD emulsion is widely used in papermaking industry to impart hydrophobic behavior to the treated cellulosic substrates (Lindstrom and Larsson 2008). The typical structures used to this context are satured or unsatured fatty acids, with a dominant molecule: stearic acid. The AKD emulsions are prepared by adding a colloidal stabilizer such, as cationic starch or a cationic polymer. Even if the covalent bond between AKD and cellulose is still under investigation and discussion, some methods exist to check the bounded and the unbounded AKD on cellulose fibers (Kumar et al. 2012). The model involves a 4 steps process, as presented in Figure I-24.

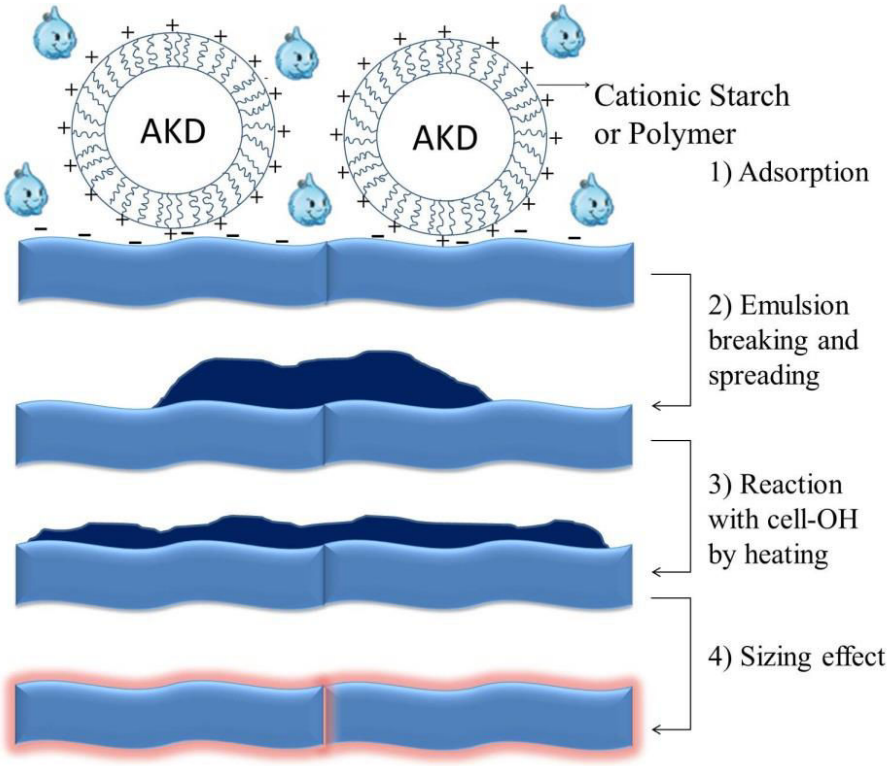


Figure I-24 : Schematic presentation of the mechanism of sizing with AKD

First, the AKD is retained in the web of paper thanks to electrostatic interactions between the anionic fibers and the cationic charge of the protective colloidal macromolecule around the AKD micelles (cationic starch or polymer). Then, in pressing and drying steps of paper, the adsorbed AKD enters in contact with the cellulose fibers and spreads. The spreading of

AKD leads to the formation of “monolayer” and finally the reaction occurred and the aliphatic tails of AKD are oriented to the air interface, thus achieving the sizing of the fiber surface.

Several reviews are available (Cunha and Gandini 2010; Zhang et al. 2007) dealing with the AKD sizing on cellulosic surface to impart hydrophobic behavior. The reaction between AKD and cellulosic fibers is well-known since 70’s. Reactions occur during modification are given in Figure I-25. Several reviews are available in literature to described the possible interactions and the modification of cellulose fibers using AKD (Lindstrom and Glad-Nordmark 2007; Lindstrom and Larsson 2008; Mattsson 2002).

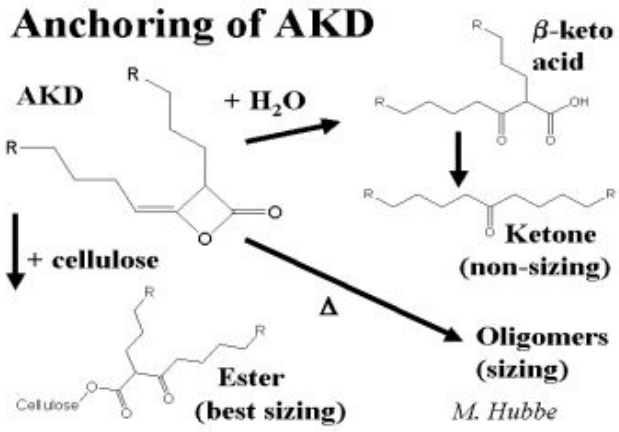


Figure I-25 : Reactions between cellulose and AKD

More recently Song et al. (Song et al. 2012) studied the interactions of AKD with cellulose in homogeneous and heterogeneous conditions. The reaction products were characterized by FTIR, SEM, TGA-DTA and WXRD. In homogeneous conditions after dissolution of cellulose fibers using DMAc/LiCl as solvent, the crystalline region of cellulose, as well as the intra and intermolecular hydrogen bonds were destroyed. FTIR showed that hydroxyl groups were able to react with AKD to generate ester bonds. In heterogeneous conditions, the activity and accessibility of free hydroxyl groups were restricted and no ester bonds were detected by FTIR. *Reaction and interactions will be investigated more deeply in the chapter section 2.3*. Other reaction can be found in literature as polymer grafting onto cellulose fibers which limits the reaction inside the fibers. This point will be detailed in next section.

As presented below, there is a lot of chemical surface reaction available in literature involving cellulose fibers. But the main raw material used during this PhD is nanofiber which is expected to exhibit different behaviors.

3. Nanofibrillated Cellulose and its modification

Two types of nanocellulose are usually considered: (i) NanoCrystalline Cellulose (NCC) and (ii) NanoFibrillated Cellulose (NFC). The preparation of NCC and NFC are completely different. Figure I-26 schematizes the main steps to obtain these two nanocelluloses from unbleached pulp.

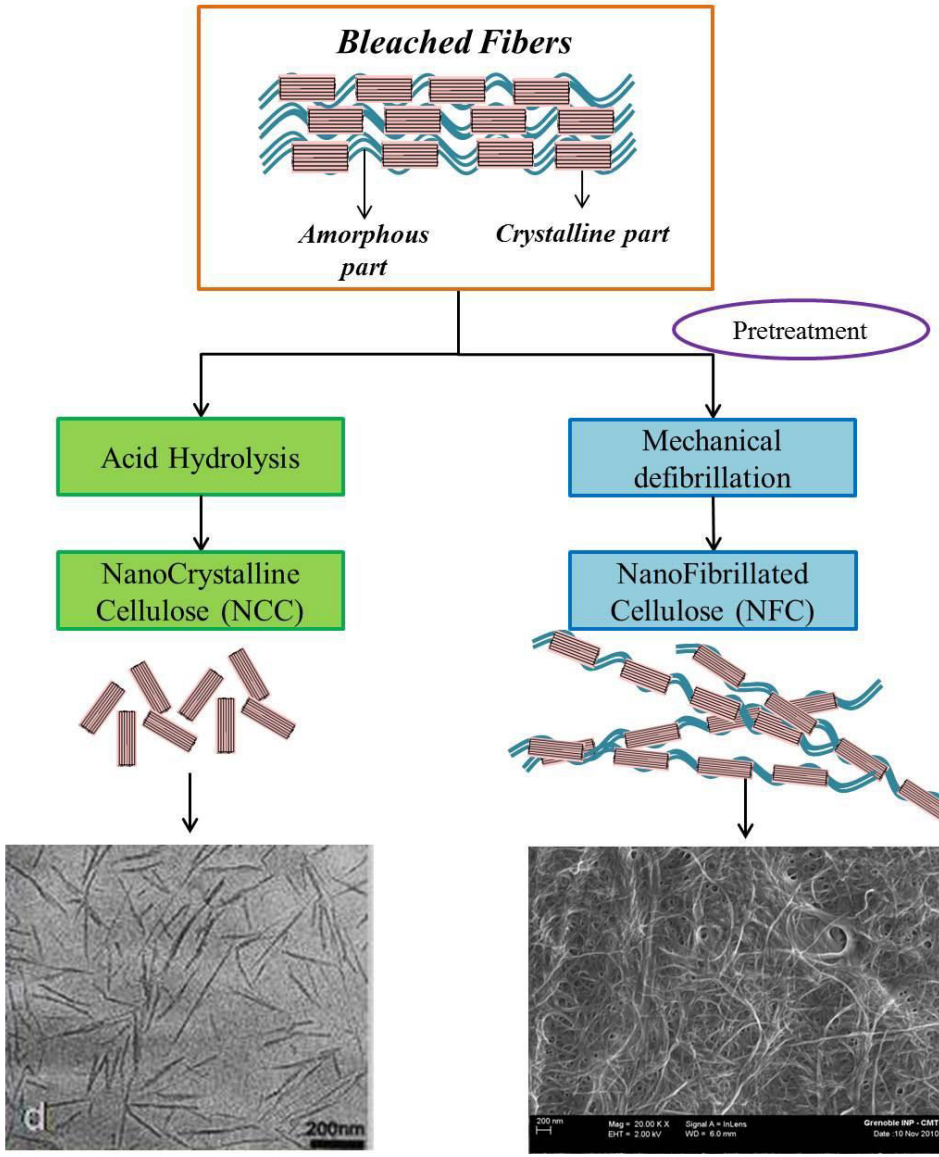
The extraction of crystalline cellulosic regions, in the form of nanowhiskers, is a simple process based on acid hydrolysis. Azizi et al. (Azizi et al. 2005) described cellulose whiskers as nanofibers which have been grown under controlled conditions that lead to the formation of high-purity single crystals. As indicated in Figure I-26, many different terms have been used in the literature to designate these nanocelluloses which enhance misunderstanding.

Concerning **NCC**, the amorphous regions are susceptible to acid attacks, and, under controlled conditions, they may be removed leaving crystalline regions intact. Beck-Candanedo (Beck-Candanedo et al. 2005) mentioned (Rånby and Ribi 1950; Rånby et al. 1949) as the pioneers in the production of stable suspensions of colloidal-sized cellulose crystals by sulfuric acid hydrolysis of wood and cotton cellulose. De Souza Lima and Borsali (De Souza Lima and Borsali 2004) described the principle of the disruption of the amorphous regions of cellulose. The hydronium ions can penetrate the material in these amorphous domains promoting the hydrolytic cleavage of the glycosidic bonds and releasing individual crystallites.

Dong at al. (Dong et al. 1998) and Beck-Candanedo et al., (Beck-Candanedo et al. 2005) studied the influence of hydrolysis time and acid-to-pulp ratio in order to obtain cellulose nanocrystals from softwood and hardwood pulps. They explained that the reaction time is one of the most important parameters to be considered. Araki et al. (Araki et al. 1998) compared the effects of using sulfuric acid or hydrochloridric acid to produce stable suspensions of cellulosic nanocrystals.

Main Reviews :
- Lin et al. (2012)
- Habibi et al. (2010)
- Hubbe et al. (2008)
- Samir et al. (2005)

Main Reviews :
- Lavoine et al. (2012)
- Isogai et al. (2011)
- Moon et al. (2010)
- Siqueira et al. (2010)
- Siro et al. (2010)
- Eichorn et al. (2010)



Key parameters :
- Sources
- Acid used
- Time of hydrolysis

Key parameters :
- Pre-treatment
- Process

Denomination in literature :
- Cellulose nanowhiskers (CNW)
- Cellulose NanoCrystals (CNXL)
- Cellulose Nanowhiskers (CNW-HCl)
- Whiskers (Wh)
- Nanocrystalline cellulose (NCC)
- Cellulose Crystallites (/)
- Nanocellulose (/)

Denomination in literature :
- Microfibrillated cellulose (MFC)
- Microfibrils of cellulose (MFC)
- Cellulose Microfibrils
- Cellulose nanofibers (CNF)
- Nanofibrils of cellulose (NFC)
- Nanofibrillated cellulose (NFC)
- Nanofibrillar cellulose (NFC)
- Tempo oxydated Cellulose Nanofibrils (TOCN)

Dimensions:
- Length 100 – 500 nm
- Diameter 5 – 10 nm

Dimensions:
- Length > 1µm
- Diameter 5 – 50 nm

Figure I-26 : Schematic representation for preparation of NCC (left) and NFC (right) starting with fibers

These authors (Araki et al. 1998) explained that sulfuric acid provides more stable aqueous suspensions than hydrochloridric acid because sulfuric acid-prepared nanocrystals present a negatively charged surface (sulfate groups).

Cellulose whiskers can be prepared from a variety of sources, e.g. microcrystalline cellulose, bacterial cellulose, algal cellulose (valonia), hemp, tunicin, cotton, ramie, sisal, sugar beet, and wood. To a certain extent, geometrical characteristics such as size, dimensions and shape of cellulose nanocrystals depend on the source of cellulose as well as the hydrolysis conditions. Typical dimensions of whiskers range from 5 to 10 nm in diameter and from 100 to 500 nm in length. Contrary to NFC, above a critical concentration, the rod-like shape of the charged cellulose nanocrystals leads to the formation of an anisotropic liquid crystalline phase. This chiral nematic organization can give coloration without any pigment and opens new challenges and applications.

NFC can be viewed as a cellulosic material, composed of expanded high-volume cellulose, moderately degraded and greatly expanded in surface area, obtained by a homogenization process. Contrary to straight cellulose whiskers, cellulose nanofibrils are long and flexible highly elongated nano-element. NFC is composed of more or less individualized cellulose nanofibrils, that present lateral dimensions in the order of 10 to 100 nm, and length generally in the micrometer scale, and consisting themselves of alternating crystalline and amorphous strings.

NFCs are the key raw materials used during this PhD so before discussing its chemical modification, their preparation and properties will be detailed in coming sub-chapters.

3.1 Generalities: Definition and preparation of NFC

3.1.1 Definitions

NanoFibrillated Cellulose (NFC) refers to cellulose fibers that have been fibrillated to achieve agglomerates of cellulose microfibrils units, as described in Chapter 1 (section 1.1). NFCs have nanoscale (less than 100nm) diameter and typical length of several micrometers. Several denominations exist for describing such material and most often MicroFibrillated Cellulose (MFC) is used. An ISO standard group is working on an international denomination and first results has been more developed during the last *TAPPI conference 2012 in Montreal (Canada)* (Bilodeau 2012; Ensor and Nieh 2012). In spite of this working group, number of denomination used is still high and is increasing. We will keep NFC (SUNPAP project denomination) as the main denomination all along this report. Nanofibrillated cellulose is described as a long and flexible cellulosic nano-material and is obtained from cellulose fiber by mechanical disintegration. Several methods are currently used and will be detailed latter, but main principle is described in Figure I-27.

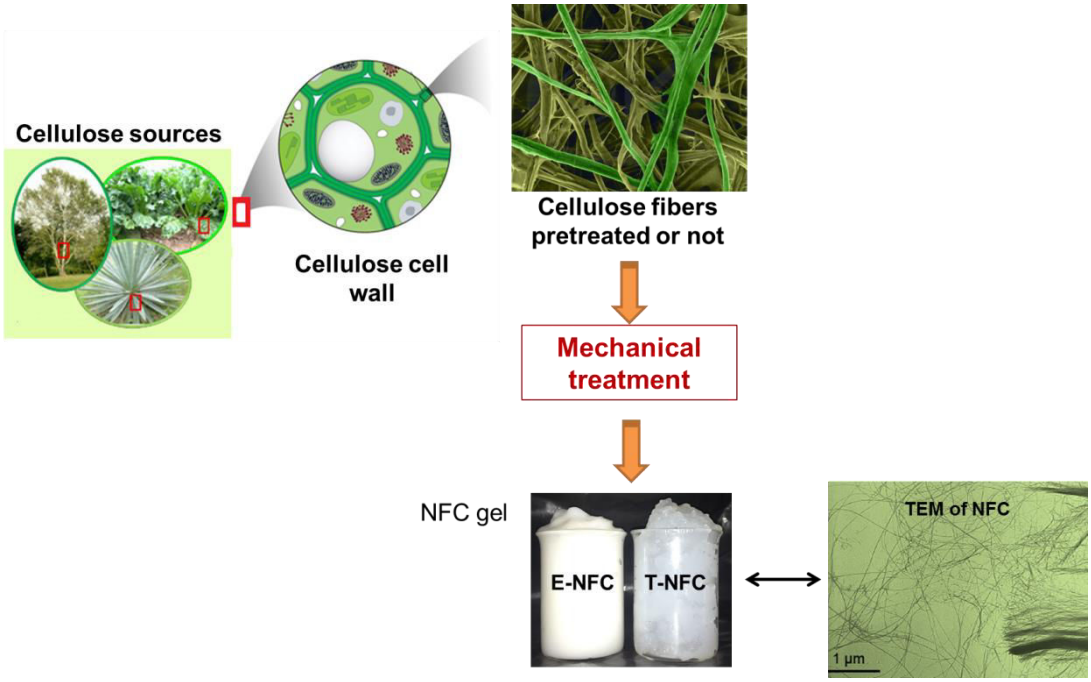


Figure I-27 : From wood to NanoFibrillated Cellulose (adapted from Lavoine et al. 2012)

Field Emission – Scanning Electron Microscopy (FE-SEM), Atomic Force Microscopy (AFM) and Transmission Electron Microscopy (TEM) analyses are usually performed to determine NFC diameters and to assess the morphology of NFC, as proposed in Figure I-28.

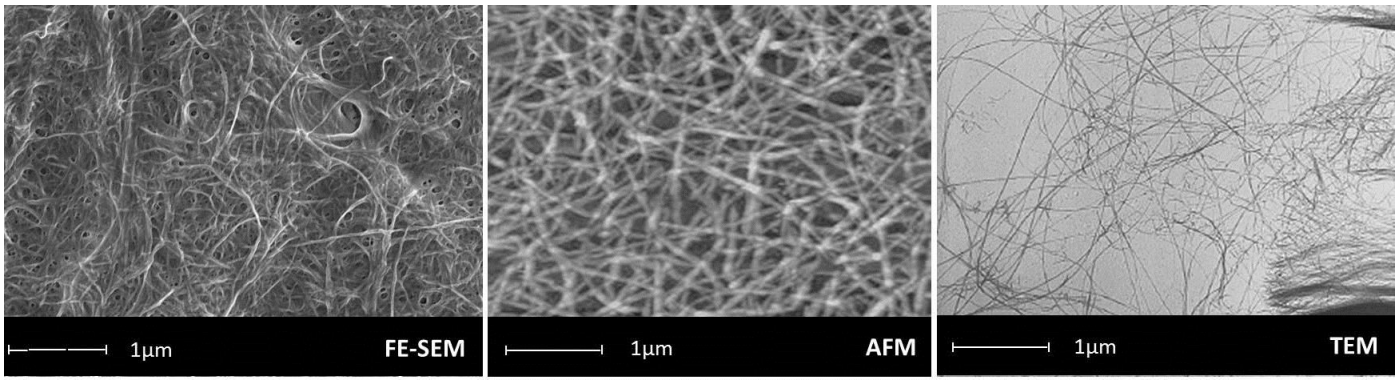


Figure I-28 : FE-SEM (Missoum et al. 2012), AFM (Innventia 2009) and TEM (Meyer et al. 2011) pictures of neat NanoFibrillated Cellulose

The first successful isolation of cellulose microfibrils was reported 30 years ago by Turbak et al. and Herrick et al. (Herrick et al. 1983; Turbak et al. 1983) using a Gaulin laboratory homogenizer. Dilute suspensions of cut cellulose fibers from softwood pulp were treated by high shear forces to yield individualized cellulose microfibrils. The resulting suspensions showed a clear increase in viscosity after several passes through the homogenizer. Indeed, NFCs tend to form an aqueous gel at very low concentration (2%wt.) due to the strong increase of specific surface area and consequently the higher number of hydrogen bonds (arising from surface hydroxyl groups) for a same volume in comparison to the native cellulosic fibers. Since 80's, other mechanical treatments have been performed and different raw materials, pre-treatments or post treatments have been tested. This will be detailed in following sub-chapters.

Nanofibrillated cellulose displays two main drawbacks, which are associated with its intrinsic physical properties. The first one is the high number of hydroxyl groups, which lead to strong hydrogen interactions between two nanofibrils and to the gel-like structure once produced. The second drawback is the high hydrophilicity of this material, which limits its uses in several applications such as in paper coating (increase of dewatering effect) or composites (tendency to form agglomerates in petro-chemical polymers). The most feasible solution to this is chemical surface modification to reduce the number of hydroxyl interactions and also to increase the compatibility with several matrices. This review details firstly the different devices and pretreatments to produce NFC followed by the surface modification of this material. To the best of our knowledge, only one review (Missoum et al. 2013) is available in this field and has been conducted in order to sum-up all the strategies available.

3.1.2 Preparation

Nanofibrillated cellulose is currently manufactured from a number of different cellulosic **sources**. Wood is obviously the most important industrial source of cellulosic fibers, and is thus the main raw material used to produce NFC. Bleached Kraft pulp is most often used as

a starting material for NFC production (Iwamoto et al. 2005; Saito et al. 2007; Saito et al. 2006a; Spence et al. 2010; Taipale et al. 2010), followed by bleached sulfite pulp (Ahola et al. 2008; Pääkkö et al. 2007; Stenstad et al. 2008). In the literature, diverse non-wood sources have already been used to produce NFC. For example, it can be extracted from sugar beet pulp (Dinand et al. 2002a; Habibi and Vignon 2008), wheat straw and soy hulls (Alemdar and Sain 2008), sisal (Siqueira et al. 2008), bagasse (Bhattacharya et al. 2008), palm trees (Bendahou et al. 2010), ramie, carrots (Siqueira et al. 2010d), luffa cylindrica (Siqueira et al. 2010a), etc. Up to date, it seems that, contrary to NCC, the raw materials have only little influence on the final NFC properties, even though they play a significant role on the processing energy consumption. Very recently, Rodionova *et al.* (Rodionova et al. 2012) analyzed more in detail 2 different bleached pulps (Norway Spruce and Eucalyptus pulps) for specifically pretreated (TEMPO pretreatment) NFC. Authors claimed that the self-standing films made from oxidized Norway spruce showed better transparency, visual appearance and tensile strength compared to the Eucalyptus pulp.

The NanoFibrillated Celluloses used in this project are obtained from a mechanical disintegration of enzymatically pre-treated the Domsjö® bleached wood pulp or Eucalyptus bleached wood pulp, as described in next section. This choice was due to the large availability of this kind of pulp in north of Europe (Finland), where, eventually, company should be built-up if the results obtained by SUNPAP co-workers are promising, according to objectives of SUNPAP project.

NFC is manufactured from a pulp suspension mainly using a mechanical treatment (Figure 2). Since the first production of nanofibrillated cellulose in the 80s, several methods have been developed to increase the production yield and the quality of the NFC. Up to now, three main families of devices have been used for the production of NFC, as presented in Figure I-29. The (i) **homogenizer system** grouping Gaulin® homogenizer machine (from APV a SPX Inc. brand, West Sussex, UK) or the GEA® homogenizer (sold by Niro Soavi, Parma, Italy); (ii) the **Microfludizer®** (developed by Microfludics Inc., Newton, MA, USA) (Figure 3); and (iii) the **grinder devices** like Masuko® systems. Each Figure is presented and the corresponding device is described.

All the first three machines are based on a high pressure homogenizing system. From a cellulose fiber suspension, the slurry is pumped through valves and injected into pistons (for Gaulin® and GEA®) or a high pressure chamber fibrillation (for microfluidizer®) around 8000 psi (55 MPa), 17,000–22,000 psi (120–150 MPa) and 10,000–30,000 psi (70–210 MPa) for Gaulin®, GEA® and Microfluidizer® machines respectively.

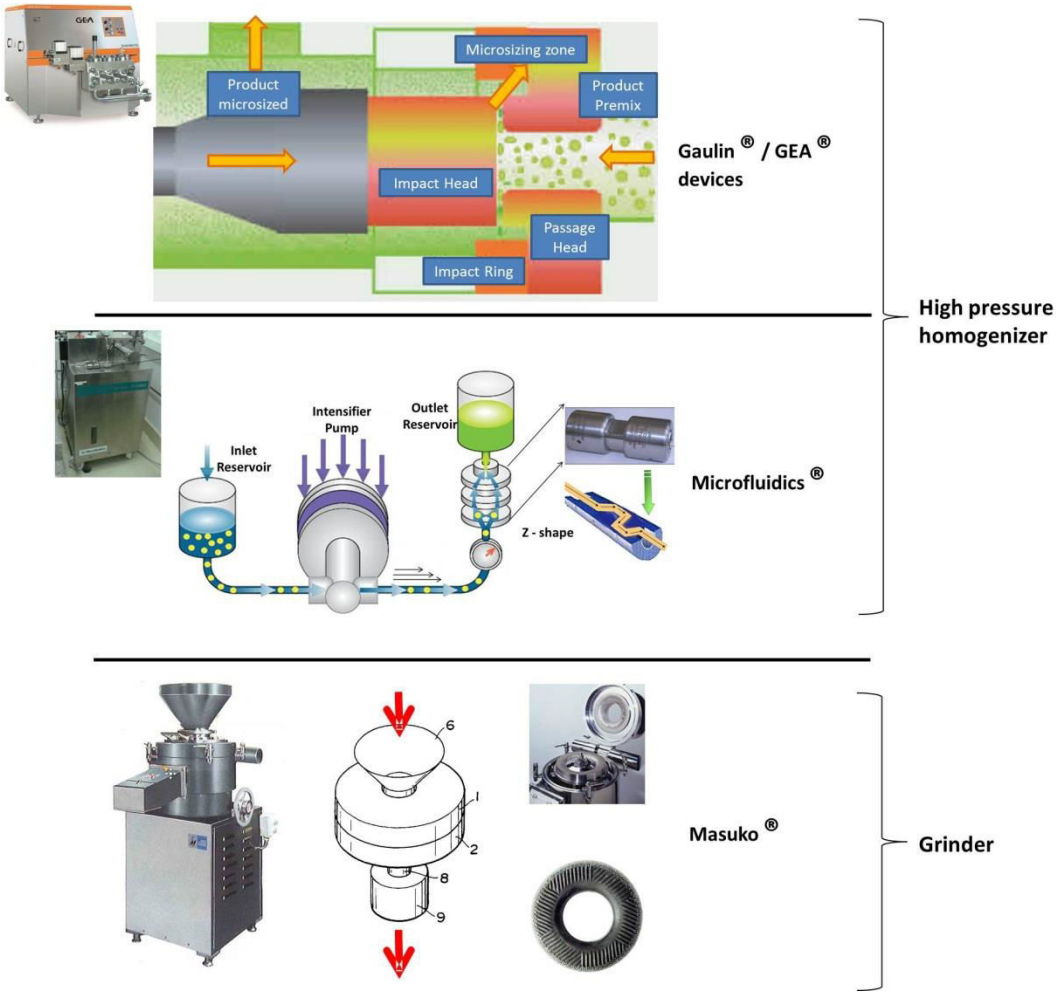


Figure I-29 : Devices available for NFC production

(i) For the homogenizer systems (Figure I-29) (i.e., Gaulin and GEA devices), the strong mechanical shearing, combined with the high pressure, initiates the fibrillation of fibers. The non-homogenized product enters into the valve area at high pressure and low velocity. The pressure is increased when pressure is applied by the pneumatic valve shaft, closing the adjustable gap between the impact head and the passage head. The homogenizing effect is caused by the product entering the valve inlet at pressure. As it passes through the minute gap, the velocity quickly increases while the pressure rapidly decreases to atmospheric pressure. The homogenized product impinges on the impact ring and exits at a sufficient pressure for moving to the next processing stage. The ensuing fibrillated fibers are cooled at room temperature. A very recent review, proposed by Lavoine et al. 2012, summarizes all the studies using such treatments before 2012 [25] as presented in Table I-6. Their review provides a new interest with development of a pilot machine like the GEA system. Before that period, the Microfluidizer was mainly used at the lab scale. We can notice that even if it is the first process studied in the 80's, 67% of scientific papers were not published at the start of our project in 2009.

Table I-6 : Pre- and post-treatments applied in literature to different sources with homogenizer as mechanical treatment (Lavoine et al. 2012)

Sources	Pre-treatment	Mechanical treatment	Post-treatment	References
Sugar beet pulp	-	Homogenizer	-	Dinand et al. EP 0726356A1, 07.02.1996
Bich hardwood cellulose				Díez et al. (2011) Macromolecular Bioscience, 11:1185-1191
Potato pulp				Dufresne et al. (1998) Macromolecules, 31:2693-2696
Kraft pulp (Norway spruce)			Acetylation	Rodionova et al. (2011) Cellulose, 18:127-134
Southern pine sulphite pulp				Franklin et al. US 4,481,077, 06.11.1984
Kraft pulp from Lodgepole Pine *(Pinus contorta)*, White Spruce *(Pinus glauca)* and Douglas-fir *(Pinus menziesii)*			-	Nakagaito et al. (2004) Applied Physics A., 78:547-552 Nakagaito et al. (2005) Applied Physics A., 80:155-159
Sugar beet pulp				Dufresne et al. (1997) Journal of Applied Polymer, 64(6):1185-1194
Fully bleached spruce sulphite pulp				Syverud et al. (2009) Cellulose, 16:75-85
Kraft pulp of Norway spruce				Rodionova et al. (2010) Cellulose, 18:127-134
Sugar beet pulp			Silylation (IPDM-SiCl)	Goussé et al. (2004) Polymer, 45:1569-1575
Sugar beet pulp Bleached kraft pulp			-	Agoda-Tandjawa et al. (2010) Carbohydrate Polymers, 80:677-686 Hult et al. (2010) Cellulose, 17:575-586
Fully bleached spruce sulphite pulp			Octadecyldimethyl(3-trimethoxysilylpropyl)-ammonium chlorid (ODDMAC)	Andresen et al. (2007) Biomacromolecules, 8:2149-2155
Fully bleached spruce sulphite pulp Bleached softwood sulphite pulp			- Silylation with chlorodimethyl isopropylsilane	Chinga-Carrasco et al. (2010) J Nanopart Res, 12:841-851 Andresen et al. (2006) Cellulose, 13:665-677
Kraft and sulphite pulp			-	Turbak et al. (ITT Industries, Inc.) CH 648 071 A5, 28.02.1985
Bleached spruce sulphite cellulose			Grafting of glycidyl methacrylate (Polymerisation reaction) Coating with hexamethylene diisocyanate + functionalization with 2 differents amines Grafting of anydrides (Diisopropylamine)	Stenstad et al. (2008) Cellulose, 15:35-45
Bleached wood pulp				Quiévy et al. (2010) Polymer degradation and stability, 95:306-314
Bleached kraft pulp *(Eucalyptus* and *Pinus radiata)*			-	Syverud et al. (2011) Carbohydrate polymers, 84:1033-1038
Unbleached and bleached hardwood and softwood kraft pulp				Spence et al. (2010) Bioresource Technology, 101:5961-5968
Kraft wood pulps after chemical treatments and TMP				Spence et al. (2010) Cellulose, 17:835-848
Bleached and unbleached kraft hardwood pulps				Spence et al. (2011) Cellulose, 18:1097-1111
Bleached kraft pulp				Wenshuai et al. (2010) Advanced materials research, 87-88:393-397
Bleached kraft pulp	Grinders comprising abrasive grains		-	Matsuda et al. US 6,183,586 B1, 06.02.2001
Elemental chlorine free (ECF) fully bleached sulphate pulp *(Picea abies)*	Cutting with an office shredder		-	Iotti et al. (2011) J Polym Environ, 19:137-145
ECF fully bleached sulphate cellulose *(Picea abies)* with up to 5% w/w pine *(Pinus sylvestris)*				
Sugar beet pulp	Waring Blender		-	Dinand et al. (1999) Food Hydrocolloids, 13:275-283
Bleached kraft pulp *(Eucalyptus* and *Pinus radiata)*	TEMPO-Mediated Oxydation		-	Syverud et al. (2011) Carbohydrate polymers, 84:1033-1038
Softwood cellulose fibers				Bilbao-Sainz et al. (2011) Carbohydrate Polymers, 86:1549-1557
Tunicate *(Halocynthia papillosa)*				Iwamoto et al. (2009) Biomacromolecules, 10:2571-2576
Fully bleached softwood kraft pulp				Xhanari et al. (2011), Cellulose, 18:257-270
Sulfite dissolving pulp (Domsjö Dissolving Plus)	Carboxymethylation		-	Mikkonen et al. (2011) Cellulose, 18:713-726
Sulfite dissolving pulp (Domsjö Dissolving Plus)				Siró et al. (2011) Journal of Applied Polymer Science, 119:2652-2660
Sulfite softwood dissolving pulp (Domsjö Dissolving Plus)				Minelli et al. (2010) Journal of Membrane Science, 358:67-75
Sulfite softwood dissolving pulp (Domsjö Dissolving Plus)				Plackett et al. (2010) Journal of Applied PolymerScience, 117:3601-3609
Wood pulp	Enzymatic		-	Wichmann (Borregaard Industries Limites) EP 2 196 579 A1, 09.12.2008
Bleached softwood sulphite pulp Wood pulps				Svagan et al. (2009) Composites Science and Technology, 69:500-506 Berglund et al. (KTH Holding AB) WO 2011/059398 A1
Bleached sulfite softwood (Domsjö ECO Bright)				Plackett et al. (2010) Journal of Applied PolymerScience, 117:3601-3609
Bleached sulfite softwood (Domsjö ECO Bright)				Minelli et al. (2010) Journal of Membrane Science, 358:67-75
Wood pulp				Holtan et al. (Boregaard Industries Limited) WO 2010/105847, 23.09.2010
Bleached kraft pulp				Wenshuai et al. (2010) Advanced materials research, 87-88:393-397
Bleached wood sulphite pulp based on Norway Spruce (*Picea abies*)				Henriksson et al.(2007) European Polymer Journal, 43:3434-3441
Bleached wood sulphite pulp based on Norway Spruce (*Picea abies*)	Acid hydrolysis (mild and strong conditions)		-	Liu et al. (2011) Biomacromolecules, 12:633-641
Wood pulp	Magnesium Chloride		-	Hamada and Bousfield (2010) TAPPI 11th Advanced Coating Fundamentals Symposium, Germany, 11-13.10.2010
Sugar beet pulp	Cryocrushing		-	Dufresne et al. (1997) Journal of Applied Polymer, 64(6):1185-1194

(ii) The microfluidizer is equipment that also allows the defibrillation of cellulosic pulps (Figure I-29). The fiber suspension is placed in an inlet reservoir, and then thanks to a pump intensifier generating high pressure, the slurry is accelerated and led into the interaction chamber. When the pressurized product enters into the interaction chamber and passes through geometrically fixed micro-channels, very high velocities are achieved. Thin Z-shaped chambers with different sizes (400–200–100 µm) have to be used for the fibrillation process. The lower the chamber size, the higher the degree of fibrillation. At the end of the process, a heat exchanger cools down the product stream to ambient temperature. Lavoine et al. 2012 give an overview of scientific works with such an apparatus (Table I-7) which has been largely performed in France and Scandinavia, place where the first well-fibrillated NFC have been studied.

Table I-7 : Pre- & post-treatments applied to different sources with microfludizer as mechanical treatment (Lavoine et al. 2012)

Sources	Pre-treatment	Mechanical treatment	Post-treatment	References
Bleached sulphite pulp	-	Microfluidizer	-	Wang et al. (2011) Biomacromolecules, 12:2074-2081
Eucalyptus sulphite wood pulp				Bilbao-Sainz et al. (2011) Carbohydrate Polymers, 86:1549-1557
Bleached *Luffa cylindrica* fibers				Siqueira et al. (2010) Bioresources, 5(2):727-740
Bleached sisal pulp				Belbekhouche et al. (2011) Carbohydrate Polymers, 83:1740-1748
Sisal fibers *(Agave sisalana)*				Siqueira et al. (2010) Cellulose, 17:1147-1158 Siqueira et al. (2011) Cellulose, 18:57-65
Sisal fibers *(Agave sisalana)*			Acid hydrolysis	Siqueira et al. (2010) Cellulose, 17:1147-1158
Sisal fibers *(Agave sisalana)*			Enzymatic	Siqueira et al. (2011) Cellulose, 18:57-65
Bleached sisal pulp			Surface chemical	Siqueira et al. (2009) Biomacromolecules, 10:425-432
Elemental chlorine free bleached hardwood kraft	Refining			Taipale et al. (2010) Cellulose, 17:1005-1020
Mixture of pine and spruce pulps				Øvrebø et al. (Borregaard Industries Limited) WO 2010/102802 A1, 16.09.2010
Bleached and unbleached kraft hardwood pulps				Spence et al. (2011) Cellulose, 18:1097-1111
Softwood sulphite pulp of spruce *(Picea abies)* and white fir *(Abies alba)*	Thermostatic reactor coupled to an inline dispersing system			Zimmermann et al. (2010) Carbohydrate Polymers, 79:1086-1093
Wheat straw *(Triticum sp.)*				
Refined fibrous wheat straw (Vitacel, Rettenmaier&Söhne GmbH&Co. KG)				
Refined beech wood *(Fagus sylvatica)* (Mikro-Technik GmbH&Co. KG)				
Refined fibrous beech wood pulp (Arbocel, Rettenmaier&Söhne GmbH&Co. KG)				
Bleached sulfite softwood (Domsjö ECO Bright)	Carboxymethylation			Henriksson et al. (2008) Biomacromolecules, 9:1579-1585
Elemental chlorine free bleached hardwood kraft pulp from Birch *(Betula pendula)*				Taipale et al. (2010) Cellulose, 17:1005-1020
Domsjö dissoliving plus (Sweden)				Aulin et al. (2010) Biomacromolecules, 11:872-882
Softwood dissolving pulp (Domsjö)				Henriksson et al. US 2010/0065236 A1, 18.03.2010
Wood pulp				Ankerfors et al. (Stfipackforsk) WO 2009/123560 A1, 08.10.2009
Softwood dissolving pulp (Domsjö)				Karabulut et al. (2011) Soft Matter, 7:3467-3474
Sulfite softwood dissolving pulp (Domsjö Dissolving Plus)				Aulin et al. (2010) Cellulose, 17:559-574
Bleached sulphite pulp				Ahola et al. (2008) Cellulose, 15:303-314
Sulfite dissolving pulp (Domsjö)				Aulin et al. (2009) Langmuir, 25(13):7675-7685
Bleached sulphite softwood dissolving pulp (Domsjö ECO Bright)				Wang et al. (2011) Biomacromolecules, 12:2074-2081
Sulphite pulp (with hemicelluloses)	Enzymatic		-	Lindström et al. (Stfipackforsk AB) W0 2007/091942 A1, 16.08.2007
Sisal fibers *(Agave sisalana)*				Siqueira et al. (2010) Cellulose, 17:1147-1158
			Acid hydrolysis	Siqueira et al. (2011) Cellulose, 18:57-65
Bleached sulphite pulp				Ahola et al. (2008) Biomacromolecules, 9:1273-1282
Bleached sulphite softwood cellulose pulp (Domsjö)				Pääkkö et al. (2007) Biomacromolecules, 8:1934-1941
Bleached softwood sulphite pulp				Pääkkö et al. (2008) Soft Matter, 4(12):2492
Softwood sulphite pulp (Domsjö)				Sehaqui et al. (2010) Biomacromolecules, 11(9):2195-2198
Softwood dissolving pulp (Domsjö)				Henriksson et al. US 2010/0065236 A1, 18.03.2010
				Henriksson et al. (2011) Composites science et technology, 71(1):13-17
Softwood dissolving pulp (Domsjö)				Henriksson et al. (2008) Biomacromolecules, 9:1579-1585
Softwood dissolving pulp (Domsjö)	TEMPO-Mediated Oxydation			Henriksson et al. US 2010/0065236 A1, 18.03.2010
Bleached kraft bamboo *(P. pubescens)*				Zhang et al. (2010) Biomass and Bioenergy, *in press*
Kraft pulp (Douglas-fir)				Johnson et al. (2009) Cellulose, 16(2):227-238
Domsjö dissoliving plus (Sweden)	Pulp with N-(2,3 epoxypropyl)trimethylammonium chloride + NaOH + Isopropanol			Aulin et al. (2010) Biomacromolecules, 11:872-882
Sulfite pulp	Sulfuric acid treatment			Zimmermann et al. (2004) Advanced engineering materials, 6(9):754-761
Bleached sulphite pulp	Treatment with an aqueous electrolyte-containing solution of an amphoteric carboxymethyl cellulose			Ankerfors et al. (Stfipackforsk) WO 2009/126106 A1, 15.09.2009

(iii) The grinder device (Figure I-29), first proposed and developed by Masuko© (Tokyo, Japan), involves the breakdown of the cell wall structure thanks to the shearing forces generated by two grinding stones with countersense rotation. The pulp is passed between a static grinding stone and a rotating grinding stone revolving at about 1500 rpm. Lavoine et al. 2012 sums-up also the different pre/post treatments applied to different cellulosic fibers to obtain NFC using a grinder device as presented in Table I-8.

Table I-8 : Pre- & post-treatments applied to different sources with Grinder as mechanical treatment (Lavoine et al. 2012)

Sources	Pre-treatment	Mechanical treatment	Post-treatment	References
Japanese Cedar *(Cryptomeria japonica)* pulp				Uetani et al. (2011) Biomacromolecules, 12:348-353
ECF-bleached birch kraft pulp				Vartiainen et al. (2011) Cellulose, 18:775-786
Bleached hardwood pulp				Spence et al. (2011) BioResources, 6(4):4370-4388
Never - dried holocellulose *pulp (Sitka spruce, Picea sitchensis Carr.)*				
Once - dried holocellulose pulp *(Sitka spruce, Picea sitchensis Carr.)*	-			Iwamoto et al. (2008) Biomacromolecules, 9:1022-1026
Never - dried alkali treated pulp *(Sitka spruce, Picea sitchensis Carr.)*				
Once - dried alkali-treated pulp *(Sitka spruce, Picea sitchensis Carr.)*		Grinder	-	
Wood pulp *(Pinus radiata)*				Iwamoto et al. (2007) Applied Physics A, 89:461-466
Wodd powder from Hinoki cypress *(Chamaecyparis obtusa)*				Abe et al. (2011) Carbohydrate Polymers, 85:733-737
Wood powder *(Pinus radiata)*				Abe et al. (2007) Biomacromolecules, 8:3276-3278
Bleached and unbleached kraft hardwood pulps	Refining			Spence et al. (2011) Cellulose, 18:1097-1111
Wood powder from Douglas fir *(Pseudotsuga menziesii)*	Acetylation			Okahisa et al. (2009) Composites science and technology, 69:1958-1961
Southern softwood bleached pulp	Enzymatic			Yoo et al. (2010) Ind. Eng. Chem. Res., 49:2161-2168

(iv) Other systems (Table I-9) like cryo-crushing (Alemdar and Sain 2008) refiners (Heiskanen et al. 2011a) or extruders (Heiskanen et al. 2011b) have been performed based on the same idea. But up to know, they are not at all commonly used.

Table I-9 : Pre- & post-treatments applied to different sources with other systems as mechanical treatment (Lavoine et al. 2012)

Sources	Pre-treatment	Mechanical treatment	Post-treatment	References
Bleached hardwood kraft pulp	-	Successive stirring	-	Ishii et al. (2011) Biomacromolecules, 12:548-550
Wood powder from needle fir *(Abies nephrolepis)* Moso Bamboo Wheat straw Flax fibers		Sonication		Chen et al. (2011) Cellulose, 18:433-442
Bleached southern pine kraft pulp	TEMPO-Mediated Oxydation			Li et al. (2010) Cellulose, 17(1):57-68
Kraft pulp				Li et al. (2009) Cellulose, 16(6):1025-1032
Softwood bleached kraft pulp			Alkali treatment	Fukuzumi et al. (2010) Polymer degradation and stability, 95:1502-1508
Tunicin and bacterial cellulose			Methylation	Saito et al. (2006) Biomacromolecule, 7(6):1687 - 1691
Fully bleached softwood kraft pulp Fully bleached softwood kraft pulp Bleached hardwood kraft pulp		Ultra turrax	-	Xhanari et al. (2011), Cellulose, 18:257-270 Syverud et al. (2011) J. Nanopart Res, 13:773-782 Saito et al. (2007) Biomacromulecules, 8:2485-2491
Bleached northern black spruce pulp Wheat straw Wheat straw and soy hulls	Refining Acid and alkali treatments	Cryocrushing	-	Chakraborty et al. (2005) Holzforschung, 59:102-107 Alemdar et al. (2008) Bioresource Technology, 68:557-565 Alemdar et al. (2008) Bioresource Technology, 99:1664-1671
Japanese Cedar *(Cryptomeria japonica)* pulp	-	High-speed blender	-	Uetani et al. (2011) Biomacromolecules, 12:348-353
Potato pulp		Blender + Homogenizer Gaulin	-	Dufresne et al. (1999) Journal of Applied Polymer Science, 76:2080-2092
Softwood and hardwood bleached kraft pulps	TEMPO-Mediated Oxydation	Blender-type homogenizer		Fukuzumi et al. (2009) Biomacromolecules, 10(1):162-165
		Double cylinder homogenizer		Isogai et al. (2010) Cellulose, 18(2):421-431
Softwood bleached kraft pullp		Cylinder-type homogenizer		Fujisawa et al. (2011) Carbohydrate Polymers, 84(1):579-583
Cotton		Blade agitation		Saito et al. (2006) Biomacromolecule, 7(6):1687 - 1691
Bleached sulfite pulp from *Pinus pinaster*		Waring Blendor		
Wood pulp Kraft pulp	Enzymatic	Refiner	Enzymatic + mechanical treatment (shredder or refiner)	Hamada and Bousfield (2010) TAPPI 11th Advanced Coating Fundamentals Symposium, Germany, 11-13.10.2010 Heiskanen et al. (Stora Enso Oyj) WO 2011/004301 A1, 13.01.2011
Cellulosic fibers	Chemical (hydrogen peroxide) or enzymatic	Extruder	-	Heiskanen et al. (Stora Enso Oyj) WO 2011/051882 A1, 05.05.2011
Hadwood bleached kraft pulp Cotton linters Bleached ramie fibers Spruce hollocellulose *(Picea abies)* Softwood bleached kraft pullp	TEMPO Mediated Oxidation	No mechanical treatments	-	Saito et al. (2006) Colloids and Surfaces A : Physicochem. Eng. Aspects, 289:219-225 Saito et al. (2006) Carbohydrate Polymers, 65:435-440 Isogai et al. (2011) Cellulose, 18:421-431

Without any pre-treatment, the number of passes of cellulose fibers into the fibrillation chamber is approximately 20, 10 and 5 to reach a good quality and a homogeneous fibrillation for Gaulin, GEA and Microfludizer apparatus respectively. The energy consumption is usually high and varies according to the devices used for the fibrillation. This is one of the main drawbacks related to the process of NFC production. Some pretreatments were developed by researchers in order to solve this problem and facilitate production at a larger-scale, as shown with a homogenizer.

3.1.3 Pre-treatments

Nowadays, 2 main pretreatments could be applied on cellulose fibers to produce NFC, i.e. (i) Enzymatic or (ii) TEMPO pretreatment.

(i) Enzymatic pre-treatment

Enzymatic pre-treatments enable NFC manufacture with significant reduced energy consumption. Inspired by nature, the idea is to limit interactions between microfibrils. Indeed, cellulose is degraded in nature by a set of enzymes called cellulases. They can be classified as A- and B- type cellulases, termed cellobiohydrolases, which are able to attack highly crystalline cellulose, or as C- and D-type cellulases or (endoglucanases) which generally require some disorder in the structure in order to degrade cellulose (Henriksson et al. 2005;

Henriksson et al. 1999)]. Cellobiohydrolases and endoglucanases can show also strong synergistic effects (Berghem and Pettersson 1973; Henriksson et al. 2007). During preparation of NFC, isolated cellulases can be applied to modify the structure rather than degrading the cellulose. Some authors (Henriksson et al. 2007; Pääkkö et al. 2007) found that endoglucanase pre-treatment facilitates disintegration of cellulosic wood fiber pulp into cellulosic nanofibers. Pretreated fibers subjected to the lowest enzyme concentration (0.02%) were successfully disintegrated while molecular weight and fiber length were well preserved. Between two refining steps, Pääkkö et al. 2007 performed an enzymatic treatment with endoglucanase before passing the pulp slurry through the microfluidizer which promotes cell wall delamination, and thus prevents the z-shaped chamber in the microfluidizer from blocking or clogging. They compared enzyme-pretreated NFC with non-pretreated NFC, as well as with a gentle and strong hydrolysis of pretreated NFC. Endoglucanase pre-treatment facilitates the disintegration of cellulosic wood fiber pulp by increasing its swelling in water. Moreover, this environmentally friendly pre-treatment confers a more favorable structure on the NFC, as it reduces the fiber length and increases the extent of fine material, compared to the result of acid hydrolysis pre-treatment. Their results showed that enzymatic pre-treatment gives much more homogeneous NFC suspensions. Thus, enzymatic pre-treatment is a very promising method for industrial applications and larger-scale NFC production. It is also one of the key steps in the first pilot production of NFC that was announced by Lindström's group from Innventia ("Press Release: Nanocellulose—for the first time on a large scale—Innventia," 2011).

A quite recent study that was subdivided into two scientific papers (Siqueira et al. 2010e; Siqueira et al. 2011c) gave a more detailed analysis of the impact of enzymatic treatment on the final properties of the NFC obtained. In the experiments, two kinds of enzymes at different concentrations were tested as post- and pre-treatments. The results showed the importance of precisely detailing such post- or pre-treatment. Indeed depending on cellulase concentration, the morphology of ensuing NFC and their reinforcing effect in a matrix can be totally different. The authors insist on the need for precise manufacturing protocols when discussing NFC.

(ii) TEMPO mediated oxidation pre-treatment

Currently, the more commonly used chemical pre-treatment is TEMPO-mediated oxidation. Indeed, the TOCNs, or TEMPO-oxidized cellulose nanofibers, represent an entire category of nanocellulose worthy of consideration.

TEMPO-mediated oxidation is a well-known method for modifying selectively the surface of native cellulose under aqueous and mild conditions (Saito et al. 2007; Saito et al. 2006a; Saito et al. 2006b; Saito and Isogai 2004).

The basic principle of this form of pre-treatment consists of the oxidation of cellulose fibers via the addition of NaClO to aqueous cellulose suspensions in the presence of catalytic amounts of 2,2,6,6 tetramethyl-1-piperidinyloxy (TEMPO) and NaBr at pH 10–11 at room temperature (Figure I-30). The C6 primary hydroxyl groups of cellulose are thus selectively converted to carboxylate groups via the C6 aldehyde groups, and only NaClO and NaOH are consumed.

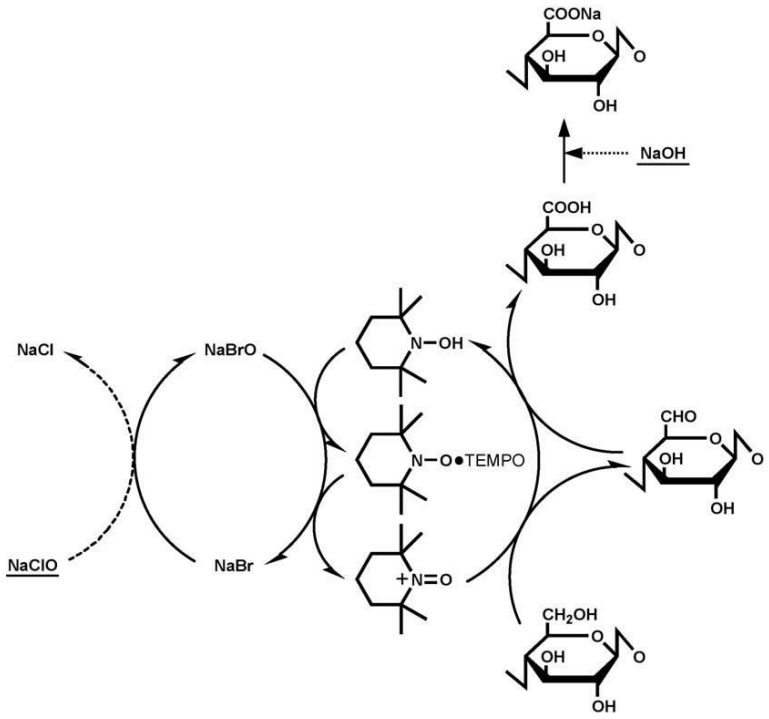


Figure I-30 : Regioselective oxidation of cellulose by TEMPO process (Isogai 2011)

The higher the quantity of NaClO in the reaction medium, the higher is the number of carboxylic groups formed at the surface of the NFC and the stronger is the decrease in the degree of polymerization (DP). Isogai's group (Saito et al. 2006a; Saito et al. 2006b) applied this treatment to many diverse sources: wood pulp, cotton linters, tunicate, bacterial cellulose, ramie, and spruce holocellulose etc. They defined the oxidation efficiency of their pre-treatment by the following equation (Saito et al. 2006b):

$$\text{Oxidation efficiency (\%)} = 100 \times \{2 \times (CT - CO) + (AT - AO)\}/MNaClO$$

where M_{NaClO} is the quantity of NaClO added (mmol/g); CO and CT are the carboxylate contents (mmol/g) before and after oxidation, respectively, and AT and AO are the corresponding aldehyde contents (mmol/g), respectively.

Another TEMPO-mediated oxidation system has been reported with different conditions in comparison to the first one. This system operates at pH 7, NaClO replaces NaBr, and the primary oxidant is $NaClO_2$ instead of NaClO.

Recently, a TEMPO electro-mediated reaction was also developed as an alternative method to oxidize the C6-primary hydroxyls of cellulose (Isogai et al. 2011b). The authors applied two new systems to softwood bleached Kraft pulp: electro-mediated oxidation with TEMPO at pH 10, and 4-acetamido-TEMPO at pH 6.8 in a buffer solution. This new sustainable method could well replace the first two systems, although longer oxidation times are required. The yield is quite high (more than 80%). Moreover, it preserves the main characteristics of TEMPO-oxidized NFC produced from bleached softwood Kraft pulp (Isogai et al. 2011b) or from annual plant (Sbiai et al. 2011).

More details about TEMPO treatment, processes and application are summarized in a very recent review paper by Isogai (Isogai et al. 2011a).

Even if the washing step of these tempo-treated fibers is still the main drawback for their industrialization, they have several advantages. Indeed, compared to the energy consumption of repeated cycles of a high pressure homogenizer (700–1400 MJ/kg), TEMPO-mediated oxidation pre-treatment drastically decreases the consumption to values less than 7 MJ/kg. The nanofibrils within the fibers separate from each other more easily due to the repulsive forces of the ionized carboxylate groups, which overwhelm the hydrogen bonds holding them together (Eichhorn et al. 2010). TEMPO oxidation pre-treatment is usually followed by a mechanical treatment, which can be performed using the devices mentioned before but also with a simpler system like a mixer. However, it is worth keeping in mind that, one key step in this process is the “post-separation” of smaller NFC and bigger NFC by centrifugation. Only the supernatant (smaller NFC) is usually considered as TOCN. The ensuing TOCN material is shorter and thinner than with enzymatic pretreatment which presents other properties completely different from those obtained by the enzymatic way.

(iii) Other Pre-Treatments in the Literature

Other pre-treatments exist such as carboxymethylation (Aulin et al. 2010) or acetylation (Okahisa et al. 2009) but they are less used. Lavoine et al. 2012 summarized all pre- or post-treatments and devices used to obtain NFC. The work constitutes an exhaustive list of all sources used for the production of NFC. The publication deals with NFC barriers and gives an overview of all the grades available of NFC and the influence on barrier properties.

Cellulose surface modification, as briefly discussed in the introduction, has already been studied for several applications and several reviews have given a clear overview of the different existing strategies. However, none exists regarding NFC surface modification. The next section discusses the different strategies developed to physically or chemically modify NFCs.

In our project we have used enzymatically and TEMPO pre-treated NFC for chemically grafting them. Cellulose surface modification, as presented before, has already been studied for several applications and several reviews give clear overview of different existing strategies (Belgacem and Gandini 2009; Belgacem and Gandini 2008; Belgacem and Gandini 2005).

NFC surface modification strategies will be detailed at the end of this Chapter, but before, NFC properties and application have to be described in order to understand the modification objectives and requirements.

3.2 Properties and application

There is several applications and properties target when using NFC. This NFC can be used as 100% NFC standing films, or in surface or bulk in paper and in composites. The Figure I-31 shows these potential applications.

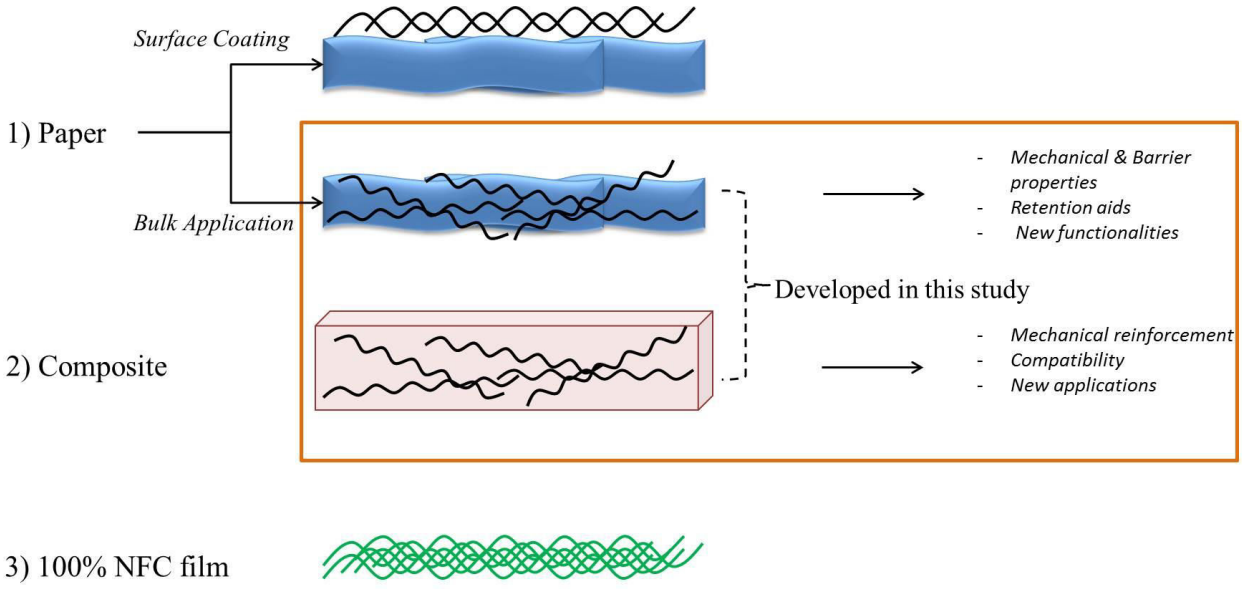


Figure I-31 : Potential application on NFC in different fields

One of the more visual properties of NFC is their capacity to form a gel at low concentration and their capacity to be converted into film either by casting (Andresen et al. 2007; Andresen et al. 2006; Dufresne et al. 1997; Saito et al. 2006b) or using a handsheet former / vacuum filtered (Henriksson et al. 2008; Iwamoto et al. 2007; Iwamoto et al. 2005; Nakagaito and Yano 2008; Nakagaito and Yano 2004; Seydibeyoğlu and Oksman 2008). When the water is removed from the NFC gel, stiffer and stronger 100% NFC standing films are formed thanks to the nanofibrillar network and interfibrillar hydrogen bonding formed during the drying process.

3.2.1 Mechanical Properties

Mechanical properties of NFC films prepared from different cellulose sources and by different procedures are summarized in Table I-10.

Table I-10 : Mechanical properties of NFC films obtained by casting or vacuum filtering (adapted from Lavoine et al. 2012)

Raw materials	Processes	Max. Stress (MPa)	E modulus (GPa)	Strain at break (%)	References
Sugar beet pulp	Casting	/	2.5 – 3.2	ND	(Dufresne et al. 1997)
Softwood sulfite pulp		80 – 100	6	1mm	(Zimmermann et al. 2005)
Bleached Softwood sulfite pulp		180	13	2.1	(Svagan et al. 2007)
Bleached sulfite softwoodpulp	Vaccum filtering	129 – 214	10.4 – 13.7	3.3 – 10.1	(Henriksson et al. 2008)
Holocellulose pulp		213 – 240	12.8 – 15.1	3.2 – 4.4	(Iwamoto et al. 2009)
Soft /Hardwood pulp bleached Kraft pulp		222-233	6.2-6.9	7.0 – 7.6	(Fukuzumi et al. 2008)
Bleached spruce sulfite pulp		104 – 154	15.7 – 17.5	5.3 – 8.6	(Syverud and Stenius 2009)

Taniguchi and Okamura (Taniguchi and Okamura 1998) were among the first whose succeeded transforming NFC suspension into homogeneous, strong and translucent films with thickness of 3–100µm by solvent casting. The tensile strength of wood pulp NFC was 2.5 times that of print-grade paper and 2.7 times that of polyethylene (PE). However, the measured tensile strength values were not specified. Henriksson et al. (Henriksson et al. 2007) reported that the mechanical properties of NFC films were reduced when immersed in water but much of the structure was retained. The nanofibers in the film were not re-dispersible in water which is due to the strong interaction between adjacent nanofibers after drying, most likely dominated by hydrogen bonding. Despite random in-plane NFC orientation, NFC films have interesting mechanical properties. As discussed by Berglund (Berglund 2006), Young's modulus may approach 20 GPa and strength can reach 240 MPa. However, most literature indicates lower modulus and strength values. Zimmerman et al. (Zimmermann et al. 2005; Zimmermann et al. 2004) reported that the tensile strength of pure NFC films almost reached the strength of clear wood (80–100 MPa) while a modulus of elasticity was found to be 6 GPa. Leitner et al. (Leitner et al. 2007) obtained values of 104 MPa and 9.4 GPa for tensile strength and modulus of elasticity respectively with cellulose

nanofibril sheets prepared from sugar beet pulp chips via solvent casting. Bruce et al. (Bruce et al. 2005) reported same values for modulus of elasticity and tensile strength (7 GPa and 100 MPa respectively) for cellulose sheets made from high pressure homogenized. More recently, Henriksson et al., in 2008, explored the structure–mechanical property relationships for pure NFC films prepared from nanofibrils of different cellulose molar mass. The porosity of the films was modified by introducing solvents other than water. The typical lateral dimensions of nanofibers were found to be 10–40 nm, suggesting that they consist of cellulose microfibril aggregates rather than smaller individual microfibrils. Despite a relatively high porosity (up to 28%) for the water-based NFC films, the Young's modulus (13.2 GPa) and tensile strength (214 MPa) were remarkably high. These values decreased significantly with increasing porosity. Assuming that NFC film is a random network of ideal straight and infinite fibers, Syverud and Stenius (Syverud and Stenius 2009) suggested that the maximum theoretical E-modulus might be one-third that of the individual fibers (i.e., 27 GPa). In reality, however, since NFC networks deviate from the ideal, significantly lower values are reported. If we compare with other materials (polymer, metals), such intrinsic properties are very high and should clearly induce mechanical reinforcement in composites. *That is why it is one of the applications studied in this project.*

3.2.2 Barrier properties

Generally speaking, it is difficult for diffusing molecules to penetrate the crystalline parts of cellulose fibrils (Syverud and Stenius 2009). Due to relatively high crystallinity (Aulin et al. 2009; Lu et al. 2008b), in combination with the ability of the nanofibers to form a dense nano-network held together by strong inter-fibrillar bonds, recently, it has been hypothesized that NFC might act as a barrier material (Syverud and Stenius 2009). Although the number of reported oxygen permeability values is limited, reports attribute high oxygen barrier properties to NFC films. They reported an oxygen transmission value of 17.75 ± 0.75 $ml.m^{-2}.day^{-1}$ for 21µm thick NFC films measured at 23°C and 0% Relative Humidity. Fukuzumi et al. 2008 reported more than a 700- fold decrease in oxygen permeability of polylactide (PLA) film when an NFC-TEMPO layer was added to the PLA surface. Similar results onto PET has been published much recently by checking pH influence.

It is hypothesized that NFC, being highly hydrophilic, tends to absorb a significant amount of moisture. Water absorption and swelling of NFC is a complex phenomenon, which is thought to be influenced both by the molecular structure of cellulose and the mesostructure of the films (Aulin et al. 2009). To the authors' knowledge only one study has been published so far presenting water uptake of neat NFC films. Belbekhouche et al. (Belbekhouche et al. 2011) compared the barrier NCC films with those of NFC films. Surprisingly, NCC films absorbed as much water as NFC films. In addition, the diffusion coefficient of NCC films was

higher than that of NFC films. Because of their more organized and highly crystalline structure, at first glance, NCC films would seem to provide more of a barrier to water. Other parameters such as entanglement and nanoporosity, can be considered as key parameters for barrier application. Some authors have reported significant porosity in NFC films (Henriksson et al. 2008; Svagan et al. 2007), which seems to be in contradiction with high oxygen barrier properties. Others authors (Aulin et al. 2012), announce very dense films which are “almost” not porous anymore. A possible explanation could be that NFC films contain closed pores in the core of the cross section and it might be inferred that good oxygen barrier properties occur as a result of close nanofiber ordering and packing as well as the effect of cellulose crystallinity. In her review, Lavoine et al. (2012) gave an exhaustive list of different sources applied and results obtained.

Table I-11 : Table comparison of barrier properties depending on the NFC type and the process applied (films, paper coated, nanocomposites) (Lavoine et al. 2012)

Raw materials	MFC fabrication process	Process	Conditions	OTR ($ml.m^{-2}.day^{-1}$)	Oxygen permeability ($mL.mm.m^{-2}.day^{-1}.atm^{-1}$)	Conditions	WVTR ($g/m^2.day$)	WVP ($g.mm/kPa.h.m^2$)	Air permeability ($nm.Pa^{-1}.s^{-1}$)
Bleached spruce sulphite pulp	MT	Films	23°C, RH 0% top side, 50% bottom side	17-18	0.352 to 0.505	-	-	-	11 to 13
BSP	MT		-	-	-	23°C, RH 50%	240 +/- 0.7	-	-
BHP			-	-	-		200 +/- 0.0	-	-
BHP	MT		-	-	-	23°C, RH 50%	2.1	-	-
BHP & Paraffin coat			-	-	-		0.4 to 0.5	-	-
BHP & Beewax coat			-	-	-		0.05 to 0.5	-	-
BHP & Cooked starch coat			-	-	-		0.5 to 1.6	-	-
Bleached wood sulphite pulp	MT		RH 0%	-	below detection limit	-	-	-	-
			RH 50%	-	0.048	-	-	-	-
			RH 95%	-	17.8	-	-	-	-
Kraft pulp	Acetylation (different reaction times)		RH 0%	5.86 to 11.1	-	23°C, RH 50%	170 to 265	-	-
	MT			4.20	-		234	-	-
	MT after complete solvent exchange			4.10	-		91.0	-	-
Bleached sulfite softwood pulp	ET		35°C, RH 0%	≈ 10^{-11} (mol.m/(m^2.s.Pa))	2.64E10^{15}+/- 0.87 (mol.m/(m^2.s.Pa))	-	-	-	-
Bleached sulfite softwood pulp	ET		23°C, RH 50%	-	0.016 +/- 0.001	-	-	-	-
Sulfite softwood dissolving pulp & Amylopectin	CT		23°C, RH 50%	-	0.013 +/- 0.005	-	-	-	-
Sulfite softwood dissolving pulp	CT		23°C, RH 50%	-	0.050 to 0.037	-	-	-	-
			23°C, RH 0 to 80%	-	6E10^{-5} to 0.085			-	-
Sulfite softwood dissolving pulp	CT			≈ 10^{-11} (mol.m/(m^2.s.Pa))	6.26E10^{15}+/- 1.27 (mol.m/(m^2.s.Pa))	-	-	-	-
BS and BH kraft pulp & PLA coat	TOCN		dry conditions	-	1 ($mL.m^{-2}.day^{-1}.Pa^{-1}$)	-	-	-	-
BSP	TOCN - NaOOH		23°C, RH 0%	-	1.7E10^{-5}	-	-	-	-
	TOCN - COOH		23°C, RH 0%	-	0.0049	-	-	-	-
Bleached wood sulphite pulp & Clay	MT	Nanocomposites	RH 0%	-	below detection limit	-	-	-	-
			RH 50%	-	0.045	-	-	-	-
			RH 95%	-	3.5	-	-	-	-
BHP & Kaolin Clay	MT		-	-	-	23°C, RH 50%	1.0 to 1.75	-	-
BHP & Calcium carbonate			-	-	-		1.4 to 2.5	-	-
BHP & Cooked starch			-	-	-		2.5 to 2.7	-	-
BHP & Uncooked starch			-	-	-		2.1 to 3.1	-	-
Bleached kraft pulp & shellac	MT		25°C, RH 50%	about 4998	-	25°C, RH 50%	about 7.45	-	0.0923
Eucalyptus sulphite wood pulp & HPMC	MT		-	-	-	about RH 81%	about 1064	0.49 to 0.70	-
	TOCN		-	-	-	about RH 82%	about 1026	0.75 to 0.79	-
Bleached sulfite softwood pulp & Amylopectin	ET		23°C, RH 50%	-	0.020 to 0.037	-	-	-	-
Sulfite softwood dissolving pulp & Amylopectin	CT		23°C, RH 50%	-	0.013 to 0.034	-	-	-	-
Bleached kraft pulp	MT	Coated paper	25°C, RH 50%	about 35000	-	25°C, RH 50%	about 63	-	0.635
Softwood pulp	CT		23°C, RH 50% Kraft paper	-	-	-	-	-	100000 to < 1
			23°C, RH 50% Greaseproof paper	-	-	-	-	-	1000 to < 0.5

3.2.3 Applications in composites

NFCs have already been added to several matrices and some book chapters or reviews have recently summarized properties and applications of such nanocomposite (Dufresne 2008; Eichhorn et al. 2010; Siqueira et al. 2010c; Siró and Plackett 2010). Since the last 3-4 years, some authors have clearly proved the strong impact of surface grafting of NFC when adding them to non-polar matrix. For example, Siqueira et al. proved that grafting fatty chains at the surface of NFC is the only way to produced PCL-based nanocomposites (Siqueira et al. 2011a). Other strategy of grafting has already been proposed (detailed later) and chemical modification is now considered as a key factor in this bionanocomposite application. However first nanocomposites were focusing on the use of water-soluble matrix or latex.

The NFC addition can improve the mechanical properties such as Young's modulus, yield strength but usually decrease the elongation. For example, the Young's modulus increase from 0.5MPa to 122MPa when 15% of NFC is added to Natural Rubber (Bendahou et al. 2010) whereas the elongation at break pass from 575 to 3.95 %. More data are available in a recent review (Siqueira et al. 2010c). Therefore, the reinforcement of transparent plastics by nano-sized fibers is considered to be promising. Indeed, very recently researchers have demonstrated experimentally the advantage of nanoscale reinforcements using nanofibrillated cellulose in combination with PVOH matrix with conservation of transparency (Srithep et al. 2012) and increasing the mechanical properties. They have notably highlighted that small quantities of nanofibers (between 2.5 and 10 %wt.) were able to reinforce the matrix, reduce the melting temperature of 5°C while maintaining light transmittance.

More recently, several researches have been focused on approaches following mono-material-based, so-called "all-polymer composites" or "self-reinforced polymer composites". All-polypropylene (all-PP) or self-reinforced polypropylene (SR-PP) composites have been proposed to replace traditional glass fibers reinforced plastics. Following the success of these all-PP composites, all-cellulose composites have been introduced. These kind of bionanocomposites turns out to be very promising, so it has been decided to focus our work on this new materials using NFC and cellulose derivatives.

Cellulose is neither soluble nor thermoplastic so , in the case of all-cellulose application, cellulose derivatives could be a smart alternative as some of them are soluble and others thermoplastics. Moreover the compatibility with cellulose should be improved. In Table I-12 some examples are given in which ethers and esters celluloses derivatives are used as matrices reinforced with NCC or NFC.

These studies will be more detailed in Chapter 3.

Table I-12 : Ethers and esters of cellulose derivatives used as matrices in composites

Matrix	Raw Materials	Method	Fillers added (wt.)	References
Hydroxypropyl cellulose (HPC)	NFC – (Refined, bleached beech pulp (RBP) Mechanical disintegration + Carboxymethylation)	Solvent casting	0, 5, 10, 20 %	(Eyholzer et al. 2011)
	NFC Tempo – (Beech wood pulp + Wheat straw pulp - Microfludizer	Solvent Casting	0, 5, 10, 20 %	(Zimmermann et al. 2010)
	NFC Never-dried kraft pulp TEMPO + high intensity ultrasonic processor	Solvent casting + Sonication time: 1, 5, 10, 15, 20min	5 %	(Johnson et al. 2009)
Hydroxyethyl cellulose (HEC)	NFC – (Softwood sulfite pulp fibers Enzymatic pretreatment + microfluidizer)	Solvent casting	0 , 12, 38, 56, 68, 100%	(Sehaqui et al. 2011)
Cellulose Acetate Butyrate (CAB)	Cellulose Nanocrystals from bacterial cellulose Sulfuric acid hydrolysis Native and silylated CNC	Solvent casting	0, 2.5, 5, 7.5, 10%	(Grunert and Winter 2002)
	Cellulose Nanocrystals from MCC Hydrochloric acid hydrolysis	Solvent Casting and solvent exchange (water to acetone)	0, 5, 10%	(Etang Ayuk et al. 2009)
	Cellulose Nanocrystals from MCC, Sulfuric acid hydrolysis	Solvent Casting	0, 5%	(Petersson et al. 2009)
	Cellulose Nanocrystals from MCC	Solvent Casting Sol-gel process	3,6, 9, 12%	(Siqueira et al. 2011b)
Cellulose Acetate (CA)	Nanofibrillated Cellulose (NFC) Kraft pulp (Pine, Spruce) Homogenizing process Neat and APS surface treatment	Solvent Casting	2.5, 5, 10%	(Lu and Drzal 2010)

3.2.4 Applications as fillers in paper

NFC can also be used in paper industry either in bulk or in surface coatings. In our study, we will focus on the first strategy (see chapter 3). More details on NFC coated paper are available elsewhere (Lavoine et al. 2012). The beneficial effect of fibers refining on the physical properties of papers is well known to all papermakers. So, it appears normal that microfibrillated cellulose or nanofibrillated cellulose could improve similarly paper physical

properties. As an example, Da Silva Perez et al., (Da Silva Perez et al. 2010) studied the influence of raw materials, pre-treatments and fibrillation conditions of nanofibrillated cellulose on their reinforcement capabilities for paper applications. Their work clearly demonstrated that the smaller and more homogeneous the NFC are, the higher the reinforcement effects are. Moreover, they showed that an addition of 1, 5 and 20%wt of NFC to a refined hardwoods and softwoods pulps could increase the tensile and tear indexes of 5 to 90% and 10% to 95% respectively. Only few information were given about the NFC retention. Figure I-32 represents typical curves obtained when reinforcing paper with NFC in term of tensile strength or Young modulus.

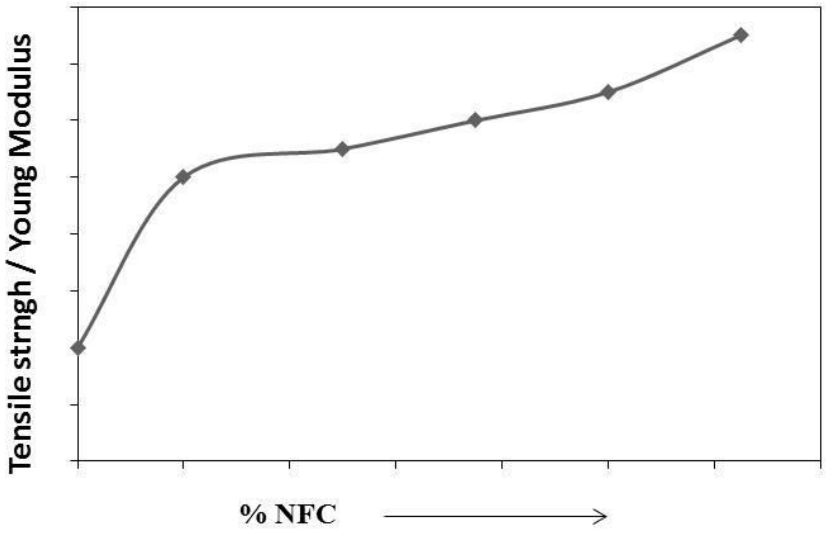


Figure I-32 : Typical curve representing tensing strength or Young Modulus of hand-sheet reinforced with NFC

Eriksen and Syverud (Eriksen and Syverud 2008) proved that addition of NFC increase the tensile index and air resistance and reduced the light scattering coefficient, opacity and brightness of the sheets.

More recently, Mörseburg and Chinga-Carrasco (Mörseburg and Chinga-Carrasco 2009) studied the potential benefits of clay and nanofibrillated cellulose in layered TMP-Based sheets. The purpose of their work was to reduce the negative effects caused by inorganic fillers on the structural properties of paper, using nanofibrillated cellulose as organic filler reinforcements. Different series of layered multi-component sheets were formed on a dynamic sheet former (DSF) with a targeted basic weight of 56g/m². A combination of retention agent and fixation agent was added in order to avoid excessive losses of fines and fillers upon sheet drainage. On the one hand it was demonstrated that NFC improve the strength properties whatever the NFC loading. On the other hand it was proven that the best way to get both better optical and mechanical properties was obtained when placing the inorganic fillers in surface layers and the NFC rather in the center of the sheet.

So, NFC can enhance strength properties of paper, but improving strength usually means increased bonding which is strongly connected to dimensional instability of paper. In their research, Manninen et al., (Manninen et al. 2011) decided to evaluate this dimensional stability of wood-free paper containing different grades of NFC. Sheets were prepared with NFC produced with a Masuko Supermasscolloider MKZA 10-15J. The authors presented retention values for NFC around 20 to 40% depending on the number of passes through the Masuko and around 90 to 100% for the mixture NFC/Starch. Indeed, a cationic starch has been added and it improved substantially the retention. In term of mechanical properties, drying shrinkage of freely dried samples increased considerably as the amount of additive was raised. When compared to the sheets containing no additives, the shrinkage was 2 times higher with 10% NFC. By the same way, hygroexpansion values of freely dried sheets rose as soon as the amount of additive increased. The cationic starch addition lowered the hygroexpansion values, the sheet containing 10% NFC with additional starch had almost the same hygroexpansion value as the sheet containing 5% NFC alone.

However, nowadays, more and more researchers are focusing on physical adsorption or chemical modifications of native NFC before addition in/on paper. The idea is to carry out surface modifications of NFC in order to bring both better properties and also new features to papers. For example, Ahola et al., (Ahola et al. 2008) worked on NFC and poly(amideamine) epichlorohydrin (PAE). Cellulose nanofibrils were used together with a cationic polyelectrolyte PAE, to enhance the wet and the dry strength of paper. Two different strategies were used to study the influence of NFC/PAE on paper properties. In the case of bi-layer strategy, PAE was first added as a 1% solution to the pulp slurry and the NFC were then added as a 0.014-0.14% aqueous solution. In the case of PAE-nanofibril-aggregates (nano-aggregates), PAE and nanofibrils were first mixed together, stirred for 5 min and then added to the pulp slurry. In the case of bi-layer system, both the wet and dry tensile strength increase significantly as the added amount of the nanofibrils increases. They proved that compared to the reference, where only 5 mg/g PAE and no nanofibrils are added, the wet strength increased more than three times when nanofibrils were used. The dry tensile strength increased 2.5 times compared to the reference. When the substances are absorbed as aggregates the wet and dry tensile indices are not increased as much as in the bi-layered system. The authors explained the unexpected results to the presence of large aggregate flocs into the paper during sheet formation. The conclusions of their work were that on the one hand, the amount of PAE needed to achieve a certain wet strength could be substantially decreased in papermaking by using NFC; on the other hand NFC achieved also high dry strength values and therefore could replace some dry strength additives that are commonly used in the paper industry. Other researchers tried to graft or modify NFC for adding new properties like antimicrobial, hydrophobic or responsive surface. Another

property added by NFC is the decrease of air permeability as firstly shown by Syverud and Stenius. (Syverud and Stenius 2009). The chemical modification could also help to control this nanoporosity.

Moreover, if we consider using NFC as (or in) coating colour on paper sheet the very high quantity of water in NFC dispersion (usually 93-98%) will be considered as a strong drawback regarding drying energy required. For all these reasons, chemical grafting of NFC is also expected in this paper field.

3.3 NFC surface modifications strategies

Due to the hydrophilic nature of cellulose, NFC cannot be uniformly dispersed in most non-polar polymer media and its suspension is a gel-like structure at very low concentration and the NFC forms films or aggregates once dried. Consequently, NFC modification is of interest in order to limit this phenomenum and open-up new applications. Compatibility with a wider variety of matrices used in coating colors or in extrusion can be attempted. NFC surface modification can also help to introduce new functionalities and to produce “active” NFC. In spite of the many methods already proposed for cellulose surface modification including a very recent review about functionalization of Cellulose Nanocrystals (Lin et al. 2012), reports on surface modification of nanocellulosic fibers are very limited in number.

The surface of cellulose nanoparticles can be modified and tuned either (i) by physical interactions or adsorption of molecules or macromolecules onto their surface or (ii) by using a chemical approach to achieve covalent bonds between cellulosic substrates and the grafting agent. Each strategy is detailed but as, a starting point, Figure I-33 gives an exhaustive overview of all reagents used for physical adsorption, as well as molecules or polymers grafted at the surface of NFC to our knowledge.

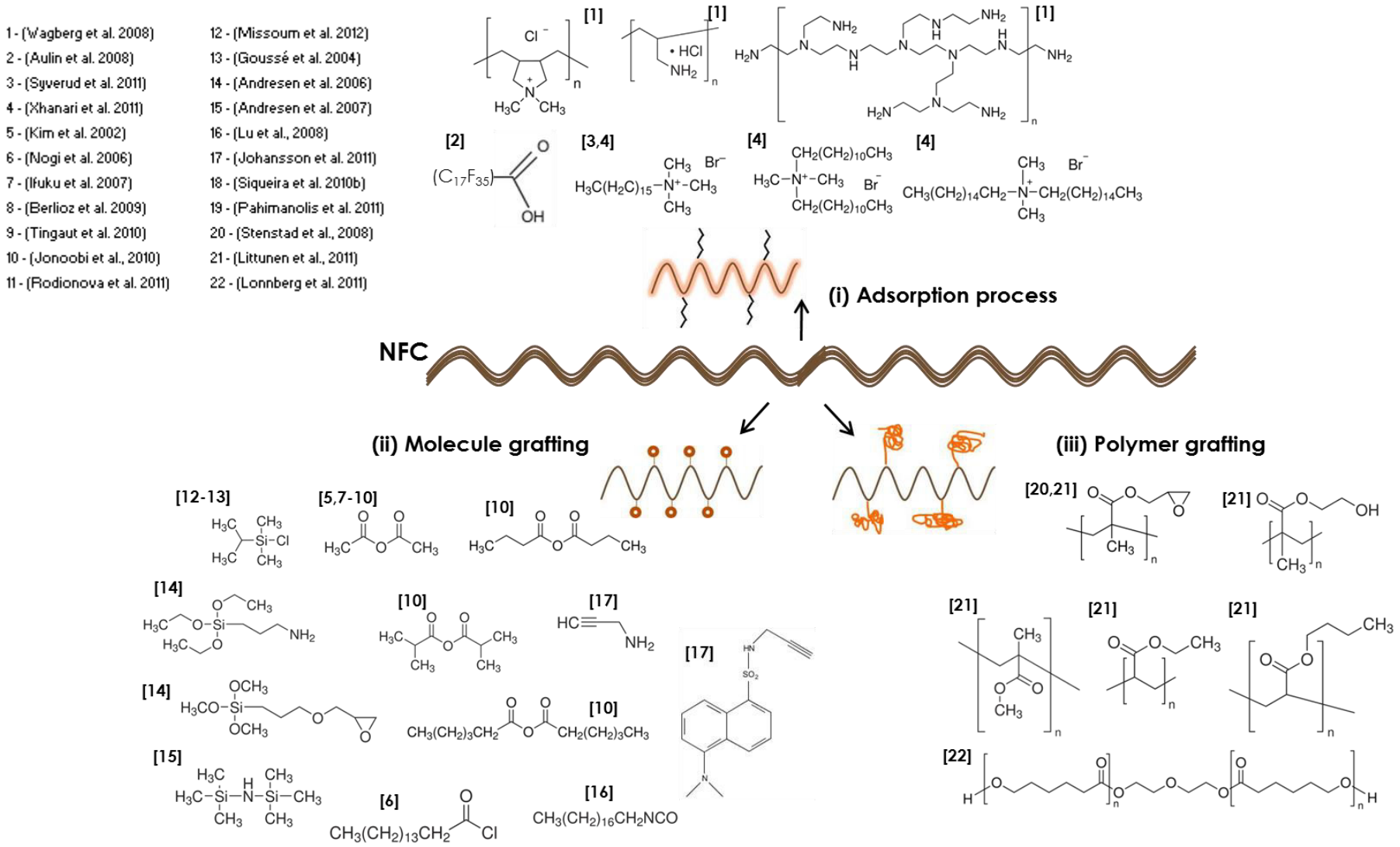


Figure I-33 : Exhaustive list of reagents used for modification of NFC. Three strategies adopted and described (i) physical adsorption,(ii) molecule surface modification and (iii) polymer grafting approaches reported in the literature (Sci Finder source updated in December 2012—the number in brackets refers to the reference number from which the information was taken.

Because of their nanoscale dimensions, nanofibrillated cellulose display a high surface area generally of the order of 50–70m2/g which greatly increase the quantity of surface hydroxyl groups available for surface modification and change the classic conditions of grafting. Moreover, the surface chemistry of NFC is primarily governed by its production procedure. Indeed, hydroxylated surfaces similar to native cellulose are classically obtained but as reported before, several strategies have been proposed to decrease the energy consumption for fibrillation. For example, TEMPO oxidation of cellulose introduces carboxylic acid groups at the surface of fibrillated cellulose. Carboxymethylation has also been used as pretreatment prior to mechanical defibrillation (Wagberg et al. 2008) and consequently also to modify the surface chemistry of the ensuing carboxymethylated NFC. Therefore, it is crucial to be precise about any NFC pretreatment when discussing NFC surface modification strategy. For example, the two latter NFCs are well adapted to the physical adsorption strategy first detailed below.

3.3.1 Surface adsorption on NFC

The surface of cellulose nanoparticles can be tuned by using surfactants or polyelectrolyte adsorption. Surfactants are usually amphiphilic organic compounds, i.e., compounds containing both hydrophobic groups (so-called tails) and hydrophilic groups (so-called heads). Cellulose films prepared from carboxymethylated NFC were modified by coating with various amounts of a fluorosurfactant, such as perfluorooctadecanoic acid ($C_{17}F_{35}COOH$) (Aulin et al. 2008). The authors demonstrated a strong decrease of dispersive surface energy after adsorption in comparison to carboxymethylated NFC, from 54.5 mN/m to 12 mN/m respectively.

The anionic surface of TEMPO-NFC can be easily modified with a cationic surfactant. As an example N-hexadecyl trimethylammonium bromide (also called cetyltrimethylammonium bromide CTAB) dissolved in water was deposited on the surface of NFC films (Syverud et al. 2011; Xhanari et al. 2011). The adsorbed layer of CTAB was found to increase the hydrophobicity of the film without affecting its mechanical properties significantly. CTAB, as well as didodecyl- (DDDAB) and dihexadecyl ammonium bromide (DHDAB) were used to control the water repellency of cellulose nanofibrils (Xhanari et al., 2011). In this study, the surfactant was directly added to NFC in an aqueous suspension. Contact angle values were determined to be higher for TEMPO-NFC film dipped in CTAB solution in comparison to neat TEMPO-NFC film (60° and 42° respectively). The treated material was not fully hydrophobic but it was rendered more water repellent (lower adhesion with water). FE-SEM characterization was done on a covered filter paper with the mixture NFC-Tempo + CTAB (Figure I-34).

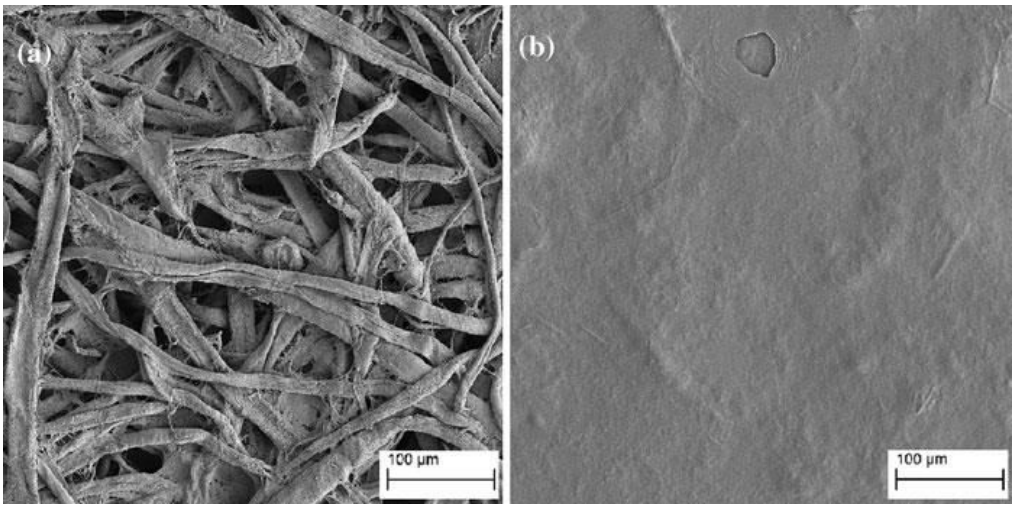


Figure I-34 : FE-SEM picture of (a) T 00—fresh filter paper and (b) T 21—film with 0.27 mmol/g CTAB adsorbed on TEMPO 2 (adapted from Xhanari et al. 2011)

Another way to modify surface properties of NFC is to use a polyelectrolyte solution. One of the most relevant scientific papers was published by Wägberg (Wägberg et al. 2008). Indeed, they performed polyelectrolyte multilayer (PEM) using three different polyelectrolytes (Poly-DADMAC, PEI and PAH solutions). NFC used was obtained by carboxymethylation of the pulp and then homogenized. After titration the NFCs displayed a total charge of 515 µeq/g and assuming that all charges are located at the surface of the NFC, the equivalent quantity for adsorption of polyelectrolytes was then added. The combination of PEI and NFC in deionized water results in the formation of regular layers of NFC and PEI with layer thicknesses of 20 and 3 nm, respectively, after deposition of about 10 layers. By changing the salt concentration during adsorption of PDADMAC and PAH, it was possible to control the thickness of the PEM. The PEMs had different colors depending on the thickness of the multilayers and simple estimations of the thickness of the PEM from the colors, assuming dense cellulose layers, showed surprisingly good agreement with data from ellipsometry measurements. This indicates that the PEMs are basically compact films of cellulose with some cationic polyelectrolyte mixed/intercalated between the fibrils.

Very recently Martins et al. (Martins et al. 2012) proposed an innovative technique in order to produced nanopaper with antimicrobial activity using polyelectrolytes as binder between NFC and silver nanoparticles. This paper reports a Layer-by-Layer (L-b-L) assembly onto NFC with cationic polyelectrolytes (i.e., PDDA, PHA and PEI) and anionic polyelectrolyte (i.e., PSS). The adsorption of a first layer of cationic polyelectrolyte was performed on NFC, followed by a second layer deposited using PSS as anionic polyelectrolyte and finally recovered with a last layer of the same cationic polyelectrolyte. Then the Ag colloidal suspension was mixed with this modified NFC. This approach was successfully employed to impart antibacterial properties to NFC. The antibacterial activity was observed for NFC/Ag

materials against different bacteria. The activity can be adjusted by varying the amount and characteristics of NFC/Ag used as nanofiller in the papers.

In conclusion, physical adsorption can be easily performed on charged NFCs to obtain more hydrophobic behavior. However, this procedure can induce some migrations phenomena of physically adsorbed moieties. That is why processes aimed at modifying NFCs chemically were developed.

Depending on the pretreatment applied for the production of NFC (carboxymethylation or TEMPO oxidation of pulp) it is necessary to well characterize charge surfaces when adsorption procedure is considered. In this report a cationic nanoemulsion will be applied on neat NFC (without chemical pretreatments) and on TEMPO oxidized NFC. This procedure and results will be detailed in next chapter.

3.3.2 Molecule chemical grafting

The hydrophobization of the cellulose surface has usually been achieved through the well-known cellulose esterification process, which basically uses carboxylic acid, acid anhydrides or acyl chlorides as reacting agents. Esterification is a reaction that introduces an ester functional group (O−C=O) onto the surface of cellulose by condensation of the previous reagents with a cellulosic alcohol group. Acetylation is the reaction that introduces an acetyl functional group CH3-C(=O)- onto the surface of cellulose. This basic reaction is also involved in the preparation of cellulose ester derivatives, such as the well-known cellulose acetate. The main target of this strategy is to keep the nanofibrillar structure so as to graft only the NFC surface.

In our case, the target is to keep the nanofibrillar structure so to graft NFC surface only.

A non-swelling media is classically used in this heterogeneous reaction mechanism in order to maintain the structure and properties. In this case, as the reaction only occurs on the cellulose chains located on the surface of the nanoparticles, the limitation on the extent of acetylation lies in the susceptibility and accessibility of the surface, which can produce several grades of modified materials with different degrees of substitution for example. In the research from Kim et al. (Kim et al. 2002). Bacterial cellulose (BC) was partially acetylated to modify its physical properties while preserving the microfibrillar morphology using anhydrous acetic acid and toluene as solvent reaction media (which are apolar, limiting the swelling of BC). In this case, the degree of acetyl substitution had a strong influence on material properties like stiffness and deformability of the acetylated BC. Mechanical properties of BC can be tuned depending on the degree of substitution. Thermal degradation resistance or optical properties have also been reported by Ifuku et al. 2007; Nogi et al. 2006. Under an oxidative atmosphere, the acetylated BC retains transparency properties after three hours at

200 °C in comparison to untreated BC films which lost their transparency after one hour at 200 °C. In addition to the acetylation methods, another process using a gas-phase method by evaporation of a large excess of palmitoyl chloride was investigated recently (Berlioz et al. 2009). The method was developed for freeze-dried bacterial cellulose microfibrils dried by the critical point method. We have to bear in mind that this procedure to dry NFC induces some irreversible aggregates. The accessibility of hydroxyl groups at the surface can be reduced. The experimental conditions (160 °C for 4 h, 170 °C for 4/6/13 h, 180 °C for 4 h and 190 °C for 2 h), nature and conditioning of cellulose were found to be important factors controlling the extent of esterification and morphology of the grafted nanoparticles. In addition, it was observed that the esterification proceeded from the surface of the cellulosic substrate to the crystalline core. This feature was confirmed by SEM analyses, which show clearly an increase in the diameter of the microfibrils and penetration depth of the chemical modification. Based on the same idea, Rodionova et al. (Rodionova et al. 2010) used a gas-phase esterification on NFC films with trifluoroacetic acid anhydride (TFAA) and acetic acid (AcOH) with several ratios (1:2 and 2:1) at 22 °C and 40 °C for 30 min or 40 min. Main results show an increase in the contact angle value (41.2° for unmodified film and 71.2° for esterified films). This gas phase esterification seems to be an effective technique for surface modification of NFC films or NFC aggregates. However, not all OH groups are available in this case and consequently, only a slight influence is observed.

Only few studies, dealing with the esterification of the NFCs surface can be found in the literature. Tingaut et al. (Tingaut et al. 2010) used a heterogeneous catalytic method thanks to a solvent exchange of a NFC suspension from water to DMF. The final product displayed several grades of acetyl content from 1.5% to 17% of acetylated groups. Such grafted NFCs are then used in nanocomposite applications and enhance interface adhesion with matrix like poly(lactic acid) through a solvent casting approach in chloroform. The authors showed that NFC with increasing percentage of acetylation (%Ac) provided more translucent nanocomposites with reduced hygroscopicity and improved thermal stability in comparison to unmodified NFC (Figure I-35). All these properties could be fine-tuned through an accurate control of %Ac.

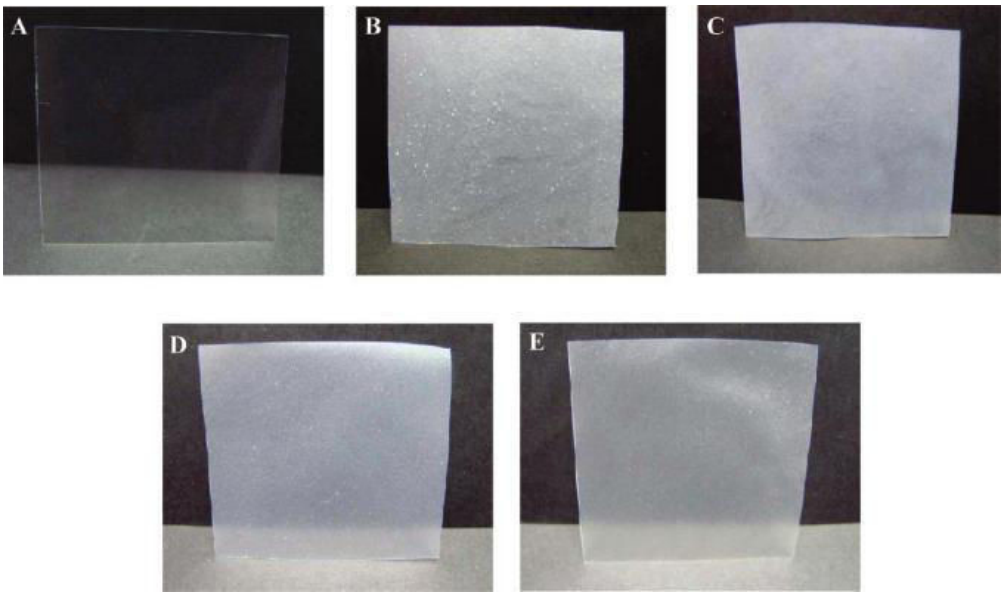


Figure I-35 : Photograph of a neat PLA film (A) and nanocomposite PLA films reinforced with 10 wt % acetylated MFC with %Ac of 0 (B), 3.5 (C) 8.5 (D), and 17% (E) (adapted from Tingaut et al. 2010)

A second study concerned acetylation onto bleached cellulosic fibers (Jonoobi et al. 2010) before mechanical disintegration. This facilitated the production of NFCs with high DS (1.07) and contact angle value (114°). It means that the fibers and thus the nanofibers are strongly modified and not only at the surface due to the decrease of the crystallinity index of the nanofibers from 81.2 to 74%. Rodionova et al. (Rodionova et al. 2011) used acetylation to increase the barrier property of NFC films with a contact angle value around 82° obtained for a DS of 0.7 for 1h of reaction. The main results of these acetylated NFC films showed no significant changes to the mechanical properties but the oxygen transmission rate was comparable to those of common packaging materials.

In our study we have developed a novel method for the chemical surface esterification of NFC in order to impart hydrophobic properties by using solvent exchange, ionic liquid and anhydrides. More details will be given in the Chapter 3.

A novel method for chemical surface esterification of NFC in order to impart hydrophobic properties by using solvent exchange in ionic liquids was recently developed by Missoum et al., in 2012 (Missoum et al. 2012) using anhydrides. Results obtained proved that the chemical surface modification occurred only at the surface of the NFC. This characterization was possible thanks to the use of a powerful technique SIMS (Secondary Ion Mass Spectrometry).

Similarly to acetyl chloride, chlorosilane has been used for NFC modification. Silylation consists of the introduction of substituted silyl groups R_3Si onto the surface of cellulose nanoparticles.

Goussé et al. 2004, utilized isopropyl dimethylchlorosilane in toluene (after solvent exchange steps) for surface silylation of cellulose nanofibrils. These authors claimed that nanofibrils retained their morphology under mild silylation conditions and could be dispersed in a non-flocculating manner into organic solvents. Andresen et al. (Andresen et al. 2000) hydrophobized NFC via partial surface silylation using the same silylation agent and reported that when silylation conditions were too harsh, partial solubilization of NFC and loss of nanostructure could occur. Films prepared from modified cellulose by solution casting showed a very high water contact angle (117–146°). It is probable that in addition to the decreased surface energy, the higher surface roughness (as a result of less hydrogen bonding) could contribute to increased hydrophobicity. It was also reported that such hydrophobized NFCs could be used for the stabilization of water-in-oil type emulsions (Andresen and Stenius 2007). More recently, Johansson et al. (Johansson et al. 2011) demonstrated the influence of solvent exchange on NFC sylilation. DMA and toluene were used as solvent for the chemical surface modification. It seems that cellulose surface adaptation can be carried out depending on the solvent used in order to minimize its free surface energy. The free, accessible hydroxyl groups generate the high surface free energy of the cellulose surface. This very recent paper launched a discussion about OH accessibility at the surface of the NFC depending on the solvent process (Figure I-36).

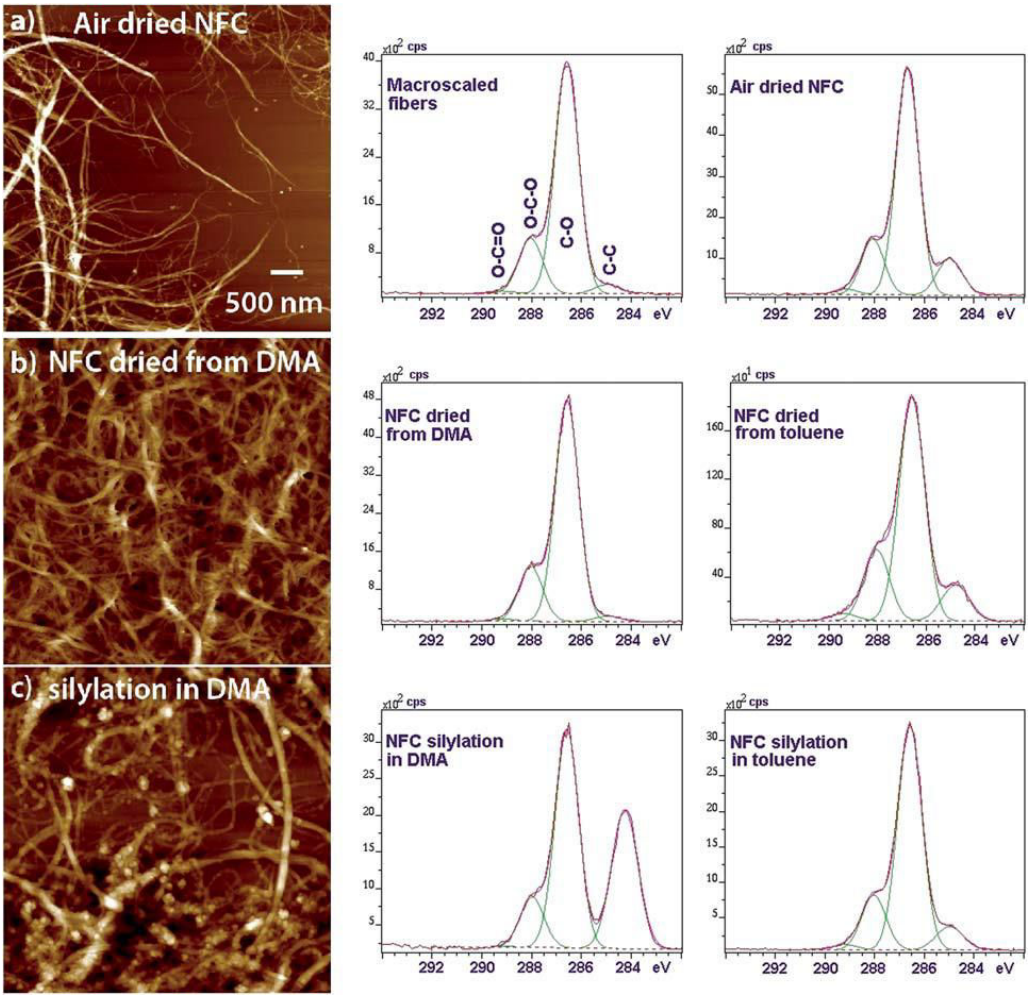


Figure I-36 : AFM and XPS data for Neat NFC and silylated NFC in DMA and toluene. Principle of the "surface adaptation" (adapted from Johansson et al. 2011)

To avoid HCl or carboxylic acid by-products obtained during these esterifications and sylilations, some carbanilations were also recently proposed. Cellulose nanofibrils extracted from sisal fibers were chemically modified with n-octadecyl isocyanate ($C_{18}H_{37}NCO$) (Siqueira et al. 2010b). The surface chemical modification was carried out in toluene using for the first time an in-situ solvent exchange procedure to avoid NFC aggregation observed previously. Never-dried NFC was grafted after solvent exchange to acetone and then to dry toluene.

Based on the same procedure, one part of our study checked the influence of different grafting agent quantities i on surface organization of grafted moieties and properties of the ensued modified NFC.

Recent strategies in aqueous media have been developed for cellulose grafting but again very few deal with NFC grafting. We can however note the use of silane and click chemistry techniques. For example, hydrophobization of NFC was also obtained by grafting 3-aminopropyltriethoxysilane (APS) and 3-glycidoxypropyltrimethoxysilane (GPS) (Lu et al. 2008a). NFC and coupling agents were mixed in acetone, and the mixture was filtered and

dried. After treatment, better and stronger adhesion between NFC and the epoxy polymer used as the matrix was observed, which resulted in better mechanical properties of the composite materials. Click chemistry is tailored to generate substances by joining small units together under mild conditions. One of the most popular reactions within the click chemistry concept is the azide alkyne Huisgen cyclo-addition using a copper catalyst at room temperature. First, reactive azide groups were introduced onto the surface of NFC by the etherification of 1-azido-2,3-poxypropane in alkaline water/isopropanol-mixture at ambient temperature (Pahimanolis et al. 2011). Then the azide groups were reacted with propargyl amine utilizing copper catalyzed azide-alkyne cycloaddition (CuAAC), leading to a pH-responsive 1,2,3-triazole-4-methanamine decorated NFC. Very recently, based on the same technique, Filpponen et al. (Filpponen et al. 2012) developed a generic and versatile method based on click chemistry for grafting all cellulosic substrates. They demonstrated that cellulose can be modified by exploiting the natural tendency of CMC to physically adsorb onto cellulose in aqueous medium, even after azide or alkyne functionalization of CMC. This property combined with a subsequent click chemistry reaction enabled modification of the cellulosic surfaces. Several cellulosic substrates (amorphous and nanofibrillar cellulose films, filter paper) as well as versatile modifications (protein, fluorescent labeling, and PEG grafting) were performed. This method has a potential to set an altogether alternative trend for heterogeneous modification of cellulose. The last strategy used is polymer grafting onto NFC.

3.3.3 Polymer grafting

Surface chemical modification of cellulose nanoparticles can be achieved by covalently attaching small molecules, as well as polymers. The general objective of this chemical modification is to increase the apolar character of the nanoparticle and have a better compatibility with hydrophobic polymer matrices. Two main approaches can be used to graft polymers onto surfaces, i.e., “grafting onto” or “grafting from”. The first method was extensively used for the fibers or the NCC particles and not for the NFC. The “grafting onto” approach consists of: (i) mixing the cellulosic nanoparticles with an existing polymer and a coupling agent to attach the polymer to the nanoparticle surface; or (ii) activating the cellulose substrates (or the polymer) and grafting one (or the other) onto the other one. In this approach, one cannot expect high grafting densities because of steric hindrance induced by polymeric chains. Moreover, the viscosity of the reaction medium is usually high because of the presence of macromolecular chains. However, its main advantage is that the properties of the resulting material are perfectly controlled since the molecular weight of the attached polymer can be characterized before grafting.

The second strategy, i.e., “grafting from” approach, consists of mixing the cellulosic nanoparticles or the activated cellulosic nanoparticles with a monomer and an initiator agent to induce polymerization of the monomer from the nanoparticle surface. Because of the lower viscosity of the medium and the limitation of steric hindrance, this strategy has proven to be a very effective way to create high grafting densities on the surface. However, it is difficult to control and determine precisely the molecular weight of the grafted polymer, which is usually limited to a low degree of polymerization. The quantity of homopolymer (non-grafted) is also not so easy to determine. Several studies reported the preparation of PCL-grafted cellulose nanoparticles using the “grafting from” strategy. PCL is traditionally prepared by the Sn(Oct)2-catalyzed ring-opening polymerization (ROP) of cyclic ε-caprolactone monomer. This approach was used to prepare PCL-grafted ramie (Lin et al. 2009) and native linter (Habibi et al. 2008) cellulose nanocrystals. A similar approach was used to graft PCL on the surface of NFC as represented in Figure I-37.

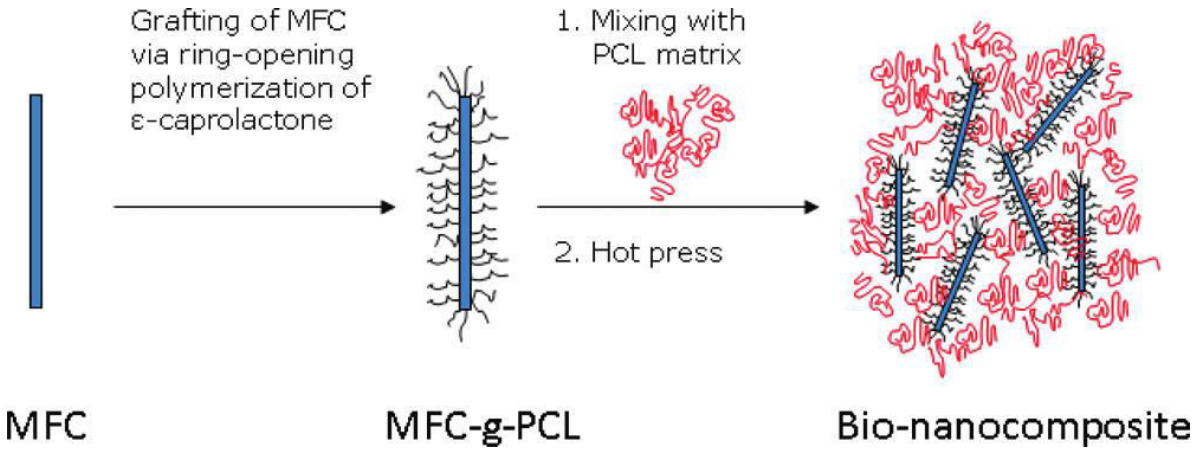


Figure I-37 : Principle to obtained Bio-nanocomposite of PCL reinforced with NFC (Adapted from Lönnberg et al. 2011)

Freeze-dried NFC was mixed with ε-CL monomer and a grafting reaction was conducted with a catalytic amount of Sn(Oct)2 at 95 °C for 18–20 h (Lönnberg et al. 2011). By changing the amount of added free initiator to monomer, the amount of PCL on the NFC surface was altered to optimize the graft length. Different theoretical lengths of the PCL chains, i.e., DP 300, 600 and 1200, were investigated. The experimental molecular weights of free PCL formed during the grafting reaction were estimated from NMR and size exclusion chromatography (SEC). As expected, the obtained values were significantly lower than the theoretical ones since the theoretical molecular weight was calculated from the ratio of added monomer to free initiator, whereas the experimental value depends on the added monomer to free initiator, as well as the number of initiating groups on the NFC surface. TGA was used

to estimate the composition of PCL-grafted NFC. PCL contents of 16%, 19% and 21% were reported depending on the amount of free initiator in the system. Crystallization of grafted PCL was observed, but because of the lower mobility of these chains compared to free PCL, a lower melting point and degree of crystallinity, as well as a longer crystallization time were reported.

Another possibility of “grafting from” is to use classical radical polymerization thanks to a redox initiated free radical system such as Cerium Ammonium Nitrate (CAN). The cerium (IV) ion is a powerful oxidant agent for an alcohol containing 1,2-glycol groups. The mechanism of ceric ion reaction involves the formation of a chelate complex that decomposes to generate free radicals on the cellulose backbone. Epoxy functionality was introduced onto the surface of NFC by oxidation followed by radical polymerization by Cerium (IV) of glycidyl methacrylate (GMA) (Stenstad et al. 2008). Significant degradation of the cellulose chains occurred because of the formation of radicals in the reaction involving ammonium cerium nitrate. However, it was shown that the treatment resulted in only a slight reduction in the molecular weight of cellulose. In the same study, Stenstad et al. (Stenstad et al. 2008) demonstrated that the coupling of NFC with maleic anhydride introduced vinyl groups that could be used as a starting point for grafting reactions for monomers that are insoluble in water, as an alternative to the cerium-induced grafting method. NFC was also grafted in aqueous solution using a redox-initiated free radical polymerization with two acrylates and three methacrylates (Littunen et al. 2011). Cerium ammonium nitrate was also used as initiator. The graft copolymerization was dominant over homopolymerization for all monomers. The highest graft yield was obtained with butyl acrylate (BuA) and glycidyl methacrylate (GMA) with 80 wt%. According to AFM imaging, the nanofibrillar structure of the cellulose was preserved during synthesis, which means that the polymeric modification occurred without significant nanofibril aggregation. Another drawback of this grafting strategy is the high amount of homopolymer formed and the difficulty to distinguish it from the grafted polymer.

For this reason, we did not focus on this strategy during our study.

Table I-13 gathers the chemical surface modification onto NFC. All of them are very recent and half of them have been published during our project. Among the research published before our project start, we can have some doubt about quality of NFC used. Indeed, NFC production has clearly evolved during the last 3 years.

All physical and chemical strategies used to impart grafting onto Nanofibrillated Cellulose (NFC)

Table I-13 : All physical and chemical strategies used to impart grafting onto Nanofibrillated Cellulose (NFC)

Source of Cellulose	Pretreatment	Reagent	Solvent / Process	DS*	Reference	Before SUNPAP project
Surface adsorption						
Sulfite softwood dissolving pulp	Carboxy-methylation	Poly-DADMAC / PEI / PHA	LbL assembly	Surf.Charge 515µeq/g	(Wagberg et al. 2008)	Yes
Sulfite softwood dissolving pulp	Carboxy-methylation	Perfluoro-octadecanoic acid	Coating on films	nd.	(Aulin et al. 2008)	Yes
Softwood bleached Kraft pulp	TEMPO oxidation	CTAB surfactant	Coating on films	nd.	(Syverud et al. 2011)	No
Softwood bleached Kraft pulp	TEMPO oxidation	CTAB / DDDAB / DHDAB surfactant	Mixing	0.08 – 0.27	(Xhanari et al. 2011)	No
Molecule chemical grafting						
Bacterial Cellulose	*Acetobacter xylinum*	Acetic anhydride	Acetic acid + toluene	0.04 – 2.77	(Kim et al. 2002)	Yes (not our raw material)
Bacterial Cellulose	nc.	Acetic anhydride	No solvent	nd.	(Nogi et al. 2006)	Yes (not our raw material)
Bacterial Cellulose	*Acetobacter xylinum*	Acetic anhydride	Acetic acid + toluene	0.15 – 1.76	(Ifuku et al. 2007)	Yes (not our raw material)
Bacterial Cellulose	*Nata de coco*	Palmitoyl acid	Gas phase	1.47 – 2.01	(Berlioz et al. 2009)	Same time (not our raw material)
Bleached sulphite wood pulp	nc. (Supplied by Borregaard)	Acetic anhydride	DMF	%Ac. 1.5 – 17	(Tingaut et al. 2010)	No
Kenaf Bast Fibers	Acetylation	Acetic anhydride	Pyridine	1.07	(Jonoobi et al., 2010)	No
Norway Spruce Kraft Pulp	No	Acetic anhydride	Toluene	0.56 – 0.91	(Rodionova et al. 2011)	No
Sweden Domsjö Pulp	Enzyme	Acetic / Butyric / Iso-butyric / Hexanoic anhydride	bmimPF_6 Ionic liquid	0.3/0.3/ 0.2 / 0.3	(Missoum et al. 2012)	No

Table I-13 (*cont.*): All physical and chemical strategies used to impart grafting onto Nanofibrillated Cellulose (NFC)

Sugar Beet Pulp	No	Isopropyl dimethylchlorosilane	Toluene	DSS = 0.025 – 0.36	(Goussé et al. 2004)	Yes
Bleached Spruce Sulfite Cellulose	nc. (Supplied by Borregaard)	Chlorodimethyl isopropylsilane	Toluene	DSS = 0 – 0.16	(Andresen et al. 2006)	Yes
Bleached Spruce Sulfite Cellulose	nc. (Supplied by Borregaard)	Chlorodimethyl isopropylsilane	Methanol water	n.c	(Andresen et al. 2007)	Yes
Kraft Pulp	nc. (Supplied by Daicel)	APS or GPS	Acetone	n.c	(Lu et al., 2008)	Yes
Bleached Spruce Sulfite Cellulose	n.c	Hexamethyl disilazane	DMA or Toluene	n.c	(Johansson et al. 2011)	No
Bleached Sisal fibers	n.c	n-octadecyl isocyanate	Toluene	0.09	(Siqueira et al. 2010b)	No
Bleached Birch pulp	nc. (Supplied by Finnish center)	propargyl amine *or* 5-(dimethylamino)-N -(2-propyl)-1-naphtha lenesulfonamide	Water	0.013 0.014	(Pahimanolis et al. 2011)	No
Polymer grafting						
Bleached Spruce Sulfite Cellulose	n.c	Cerium-induced GMA	Water + HNO_3	n.c	(Stenstad et al., 2008)	Yes
Bleached Birch Pulp	n.c	Cerium-induced GMA EA MMA BuA, HEMA	Water + HNO_3	Graft yield 96-99% 81-85% 56-75% 86-89% 18-63%	(Littunen et al., 2011)	No
Bleached sulfite softwood dissolving pulp (Domsjö)	Carboxy-methylation (DS = 0.089)	PCL - $Sn(Oct)_2$-catalyzed ROP	Toluene	16-19-21%	(Lonnberg et al. 2011)	No

Regardless all the grafting strategies mentioned before, the characterization of the ensued materials is a key step in the comprehension of their properties. The use of nanoscale materials requires a precise and complete characterization. Therefore, techniques are becoming more varied and push-ups to achieve required standards in the reliability of results obtained. This is especially true and important in the present report due to the method adopted for the modification of NFC based on a **surface grafting** of this nanobiomaterials.

Regarding all strategies, few of them can be considered as green method. In this project we have focused our work on the development of new methods for chemical modification of NFC. According to the SUNPAP project, the reaction has to be the most greener as possible limiting the use of organic solvents.

4. Conclusion

Cellulose is one of the most fascinating natural polymers. It is also renewable materials largely produced by photosynthesis. It can be considered at different level with its multi-level organization and hierarchical structure. One of its promising derivatives is for sure the NanoFibrillated Cellulose. As described in this first chapter, they can be used in several applications (like papers or nanocomposites) with substantially enhanced properties. Nevertheless some drawbacks limit their uses as aggregation, low concentration suspension and compatibility with hydrophobic polymeric matrices for instance.

One solution to overcome these problems is the chemical modification of NFC. Furthermore, such an operation could be the occasion to provide new functionalities to these NFC. The surface modification of NFC is very innovative with less than 30 papers in the world and even less than 10 papers when our project has started. Up to date mainly solvent based or toxic system have been studied, which limits the extension of these finding to industrial up-scaling. This is the main reason why some European project like our SUNPAP project has been launched. In our study, the idea was to use green approach to develop and impart new properties and functionalities for these NFCs.

As described in this chapter, the chemical grafting of cellulose is well-known and some researchers have already looked for greener solutions. All of them cannot be necessary applied to NFC, like microwaves for instance. In this context, we have decided to propose 2 main original strategies of chemical grafting: (i) use of ionic liquids (which are described as green solvents) and (ii) use of water-based system (confidential). The understanding of

chemical grafting and organization of grafted moieties at NFC surface were also of interest. These 3 aspects will be detailed in chapter 2.

The chapter 3 will be then dedicated to the use of these grafted NFC within 3 different fields of applications. Indeed after the grafting of NFC some of them were applied to impart (i) antimicrobial & biodegradability properties, (ii) new functionalities to papers and (iii) reinforcement of composites.

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Figure captions

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Chapter II.

Chemical Surface Modification of NFC

Résumé Français – French Abstract

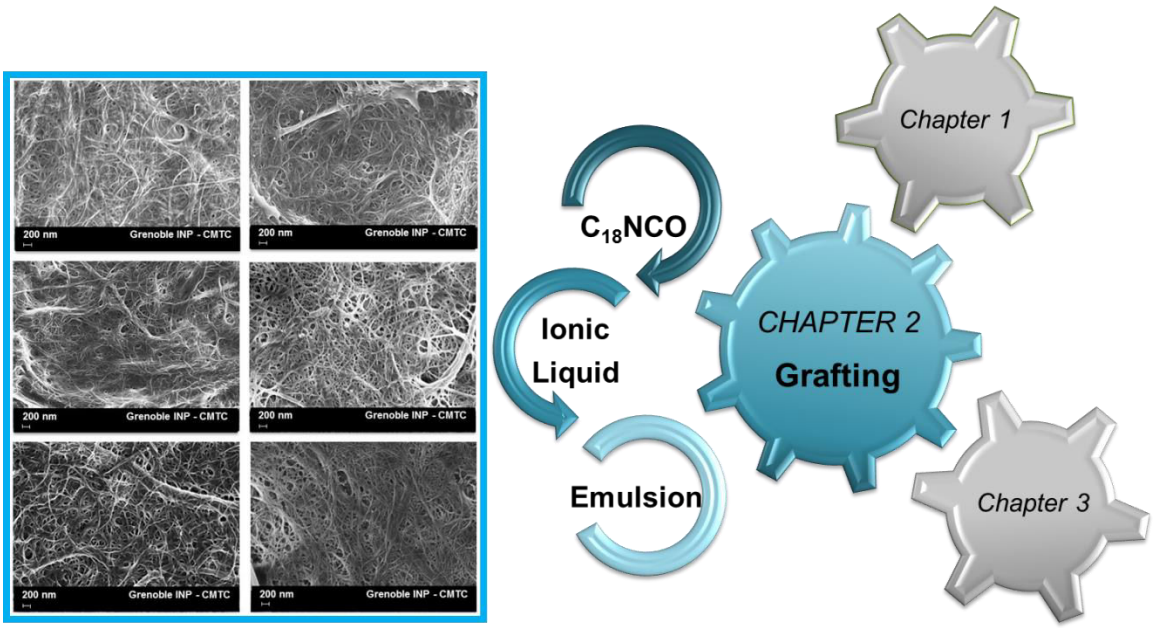

Figure 1-1 : Représentation schématique de l'organisation du projet de thèse

Comme nous venons de le voir dans le Chapitre 1, les nanofibrilles de cellulose peuvent être produites selon différentes méthodes, prétraitement et sources. Une différence majeure réside entre les NFC obtenues par le biais d'un prétraitement enzymatique ou d'un prétraitement chimique TEMPO par exemple. Leur morphologie et propriétés sont compléments différentes. Il est important de noter qu'une fois produites, les suspensions de NFC dans l'eau peuvent atteindre une concentration comprise entre 2 et 5% massique. Afin d'augmenter le taux de matière sèche de ces suspensions de NFC (ce qui serait très utile pour certains procédés), la modification chimique de surface peut être envisagée comme solution.

Dans ce Chapitre 2, nous avons voulu tout d'abord maîtriser le greffage de ces nanofibrilles de cellulose en contrôlant les effets de quantités de réactifs et en maîtrisant l'organisation et la caractérisation des greffons à leur surface. Ensuite nous avons souhaité proposé de nouvelles stratégies complétements innovantes en s'appuyant sur des solvants dits « verts » (les liquides ioniques) ou en proposant de greffer ces NFC en milieux aqueux.

Dans la première partie de ce chapitre (**Papier 1** - Publié dans *Cellulose - 2012*), un greffage de surface des NFC a été réalisé dans différentes conditions (variation du ratio molaire entre agent de greffage et groupement hydroxyle). Le protocole ainsi établi a été adapté d'après une méthode développée au sein du laboratoire et utilisée sur les nanocristaux de cellulose et les nanofibrilles de cellulose mais avec une seule quantité de greffons. L'organisation de surface de chaînes grasses obtenues par carbanilation des NFC

a ainsi pu être étudiée en détail et il a été démontrée que cette organisation influence complétement les propriétés finales des NFC.

Ces travaux montrent que les NFC peuvent être efficacement modifiées par l'emploi d'un isocyanate à chaine longue (i.e. 18 Carbones) quel que soit la quantité de greffons. La densité de greffage augmente avec l'augmentation du rapport molaire entre l'agent de greffage et le nombre de groupements hydroxyle présent à la surface de la cellulose. Grâce aux analyses XPS combinées aux analyses élémentaires des échantillons greffées, un degré de substitution interne a pu être établi pour la première fois (DSI). Il permet de quantifier les molécules greffées à la surface NFC vis-à-vis de celle qui aurait pu réagir dans la masse du matériau. L'organisation de surface de ces greffons a pu ensuite être évaluée en fonction du rapport molaire. De manière générale, les chaines aliphatiques, pour un nombre de carbone supérieur à 6-7, ont tendance à former des domaines cristallins de type cristaux liquides résultant de l'interaction latérale des chaînes aliphatiques entre elles. De ce fait, en fonction du ratio molaire utilisé lors de la réaction, des différences organisationnelles ont pu être observées grâce aux mesures XRD. La caractérisation des propriétés physico-chimiques ont démontré la présence d'un minimum à 10eq molaire due à cette organisation de surface particulière.

Toutefois, l'inconvénient majeur de ce procédé réside dans l'utilisation de solvant assez toxique (ex : toluène) mais qui est nécessaire pour éviter les phénomènes de gonflement de la cellulose. Afin de pallier à ce problème, de nouveaux solvants verts, répondant aux mêmes critères que le toluène, ont pu être développés : les Liquides Ioniques (IL). En effet, de par leur structure menant à une pression de vapeur saturante immesurable, ces solvants n'émettent aucuns composés organiques volatiles. La deuxième partie de ce chapitre (**Papier 2** - Publié dans *Soft Matter – 2012*) démontrent l'intérêt des ILs comme nouveaux solvants pouvant modifiées la cellulose.

Cette étude a clairement montré que les liquides ioniques pouvaient donner lieu à un greffage efficace des NFC avec différents greffons (anhydrides) sans modifier leurs propriétés morphologiques. De plus, il a été prouvé qu'après réaction, le liquide ionique (onéreux) est recyclable et donc réutilisable pour d'autres cycles de modifications. En outre, une technique puissante d'analyse de surface (ToF-SIMS) a été utilisée pour la première fois sur des NFC pour caractériser un greffage de surface. Ces analyses confirment le greffage de surface des NFC et démontrent l'utilité de cette technique innovante.

Il s'agit de la première étude utilisant un liquide ionique comme solvant de réaction permettant une modification de surface de la cellulose en phase hétérogène. Ces résultats prometteurs pourraient donc aider à la modification chimique de plus grand volume de NFC avec des propriétés hydrophobes. Ces dernières ont pu être utilisées pour diverses

applications dans le chapitre 3 suivant (composites ou matériaux antimicrobien). Par ailleurs, nécessitant un échange de solvants, ce greffage pourraient être d'autant plus perfectionné avec l'utilisation de NFC re-dispersable comme étudié et breveté en perspectives de ces travaux (Chapitre 4).

Malgré ces résultats prometteurs, le solvant le plus simple a manipulé (et qui évite ces échanges de solvants) reste l'eau, c'est pourquoi notre dernière stratégie s'est focalisée sur un traitement en milieu aqueux.

Dans la description de l'état de l'art, il a été présenté et discuté de deux types de NFC : une première catégorie obtenue par un prétraitement enzymatique des fibres de cellulose suivi d'un traitement mécanique et une deuxième catégorie obtenue par un traitement chimique par oxydation TEMPO.

Nous avons donc pu développer dans une troisième partie (**Papier 3** - **Soumis à confidentialité** – Dépôt d'un brevet) un dernier procédé de greffage.

Cette étude a montré que l'utilisation de l'eau comme milieu réactionnel pouvait donner lieu à un greffage des substrats nanocellulosiques sans en affecter leurs propriétés morphologiques.

Ce chapitre 2 propose donc une avancée dans la modification chimique de surface des nanofibrilles de cellulose avec des résultats prometteurs pour différentes stratégies. Il permet aussi une meilleure compréhension et caractérisation des phénomènes de greffage à cette échelle. Dans une partie ultérieure (Chapitre 3), nous étudierons et proposerons des applications basées sur ces matériaux modifiés.

English Abstract – Résumé Anglais

As discussed in Chapter 1, the cellulose nanofibrils can be produced by different methods, sources and pretreatment. It is important to note that once produced, NFC suspensions in water can reach a concentration of between 2 and 5 %wt. To increase the solid content of the suspensions NFC (which would be very useful for some processes), chemical modification of surface can be considered as a solution.

In this Chapter 2, we first tried to control the grafting of cellulose nanofibrils playing with quantities of reactants and also tried to monitor the organization of the grafts at the surface. Then we wished proposed innovative strategies for chemical grafting: either based on "green" solvents (ionic liquids) or on grafting NFC in aqueous media.

In the first part of this chapter (**Paper 1** - Published in Cellulose - 2012), a surface grafting of NFC was performed under different conditions (variation of the molar ratio of grafting agent comparing to hydroxyl groups). The procedure established was adapted from a method developed in our laboratory and using on cellulose nanocrystals and cellulose nanofibrils only one amount of reagents. The organization of fatty chain at the surface obtained by carbanilation of NFC has been studied in detail and it has been demonstrated that the organization influences strongly the final properties of NFC. Surprisingly, properties did not increase regularly but a minimum is assessed at 10eq. It is linked to the surface organization proposed and best results were obtained either with 1eq or with 30 eq of reagents.

The major drawback of this method (like most of published one) is linked to the use of toxic solvent like toluene which is necessary to avoid the swelling of cellulose. To overcome this problem, new green solvents, with the same criteria than toluene, have been chosen: a type of Ionic Liquids (ILs). Indeed, by their structure leading to an immeasurable vapor pressure, these solvents emit no volatile organic compounds. The second part of this chapter (**Paper 2** - published in Soft Matter - 2012) demonstrates the possibility of using ILs as new solvents for cellulose heterogeneous modification. This study clearly showed that ionic liquids could lead to an effective grafting of NFC (performed with several anhydrides) without changing their morphological properties. In addition, it was shown that after reaction, the ionic liquid (expensive) is recyclable and hence reusable for other cycles of reaction. In addition, a powerful technique for surface analysis (ToF-SIMS) was used for the first time on

NFC to characterize the surface grafting. These analyzes confirm the grafting surface of NFC and prove the principle of this innovative technology.

This is the first study using ionic liquid as a reaction solvent to a surface modification of the cellulose in the heterogeneous phase. These promising results may therefore help in the chemical modification of larger amount of NFC displaying hydrophobic properties. These have been used for various applications in the following Chapter 3 (like composites material or anti-microbial).

Despite these promising results, the easiest workable solvent (which avoids the solvent exchanges) is water, which consists in our last strategy for chemical grafting of NFC in aqueous based medium.

As proposed in the state of the art, it was presented and discussed two types of NFC: a first category obtained by enzymatic pretreatment of cellulose fibers, followed by mechanical treatment and a second category obtained by treatment chemical TEMPO oxidation. The major difference (chemically speaking) is the presence of carboxyl group higher after oxidation of cellulose fibers (second category).

So we have developed in the third part (**Paper 3** – **Confidential** – Patent in progress) based on water reaction media.

This chapter 2 proposes step forward results in the chemical modification of the surface of cellulose nanofibrils. It tests as pioneer promising environmentally-friendly strategies and it allows a better understanding and characterization of grafting phenomena at this scale.

In a later section (Chapter 3), we will investigate and propose some applications based on these modified NFC materials.

Chapter II.

1. Organization of aliphatic chains grafted on nanofibrillated cellulose and influence on final properties

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Abstract

Chemical surface modification of nanofibrillated cellulose (NFC) was performed using a long aliphatic isocyanate chain. Different molar ratios of the coupling agents were tested, i.e., 1, 10, 30 equivalents with respect to hydroxyl groups of the NFC surface. FE-SEM analyses revealed that there were no changes in their morphology thus keeping nanofibril-like structure with about 30 nm of diameter. All these samples were characterized by different techniques (e.g. FTIR) to check the efficiency of the grafting. Hydrophobic NFC were achieved whatever the grafting agent ratio. The Degree of Substitution (DS) was determined by Elemental Analyses and the Degree of Substitution of the Surface (DSS) was calculated thanks to X-ray Photoelectron Spectroscopy (XPS) data. Combining these two techniques, the Internal Degree of Substitution (DSI) was proposed for the first time. It indicates if the modification occurs also within NFC internal layers. Surface (contact angle), rheological (water suspension viscosity) and thermal properties (ThermoGravimetric Analysis) of grafted NFC do not follow the expected linear evolution of properties with the increase of molar ratio. X-Ray Diffraction analyses showed that the grafted aliphatic chains display crystalline waxy domains at some ratios. A model for aliphatic chain organization at the surface is proposed and clearly explained for the first time why a compromise in molar ratio is necessary to achieve best properties.

Keywords

Nanofibrillated Cellulose (NFC), Chemical surface modification, Aliphatic chain organization, Degree of Surface Substitution (DSS), thermal properties

***Inspired from**: Karim Missoum, Naceur Belgacem, Julien Bras – Cellulose (2012) – Accepted*

1.1 Introduction

The last decade has been focused on obtaining efficient material from cellulose with a very strong interest on nano-scaled cellulose-based elements. There are two main families of nano-cellulose: the cellulose nano-crystals (or whiskers) obtained by acid hydrolysis of a cellulose-rich substrate and the cellulose nanofibrils (or NFC) obtained by different combinations of enzymatic, chemical and/or mechanical treatments of these starting raw materials. Very recent reviews give detailed information for each material (Habibi et al. 2010; Siró and Plackett 2010) and emphasize the out-standing impact on the mechanical properties of the ensued bionanocomposites. (Berglund and Peijs 2010; Eichhorn et al. 2010; Liu et al. 2011; Siqueira et al. 2010a). In the present work, experiments are focused on NFC. These cellulose microfibrils (MFC, NFC) were first obtained by Herrick et al. (Herrick et al. 1983) and Turbak et al. (Turbak et al. 1983) in 1983 by a mechanical disintegration of wood pulp. Such a mechanical treatment yields the production of gelly-like aqueous suspension of nanofibrils at very low concentration. The diameter of nanofibrils obtained with these processes is in the range of 10 to 50 nm, whereas the typical length is several micrometers (Chinga-Carrasco and Syverud 2010; Walther et al. 2011). Different pretreatment such as enzymatic (Pääkkö et al. 2007; Siqueira et al. 2010c; Syverud et al. 2011) or TEMPO mediated process (Saito and Isogai 2004; Saito et al. 2007, Isogai et al. 2011), have nowadays been developed to obtain more homogeneous suspension and limit energy consumption.

All cellulose nanofibrils (NFC) tend to form an aqueous gel at very low concentration (2% wt.) due to their important specific surface area and high number of hydrogen bonds arising from hydroxyl groups present at their surface. This feature handicaps their use in several applications, such as coated products (low solid content and high viscosity) or composites. In fact, it is impossible to use them at dry state without strong tendency to form aggregates or even film-like material. In order to overcome these drawbacks, different solutions are studied, but the most common one is the surface chemical modification, aiming at transforming hydroxyl groups into other functions thus limiting (or even totally avoiding) the hydrogen bonds establishment.

Over the last decade, many processes of cellulose fibers surface modification have been investigated (Gandini and Belgacem 2011). Some of the reported approaches involved the grafting of polymers onto the surface of the fibers either by “grafting from” (like Ring Opening Polymerization - ROP (Lonnberg et al. 2006; Roy et al. 2005) and Atom Transfer Radical Polymerization – ATRP (Carlmark and Malmstrom 2003; Coskun and Temüz 2005)) or by “grafting onto” (following the procedure with bifunctionnal molecule bridge (Gaiolas et al.

2009; Krouit et al. 2008; Ly et al. 2010; Paquet et al. 2010)). The other strategy consists in grafting small molecules at the surface of fibers using acid chloride, anhydrides, silanes or isocyanates. Nevertheless, even if most of these strategies have already been tested onto cellulose nanocrystals as recently reviewed (Lin et al. 2012), only few works have been reported on the grafting of nanofibrillated cellulose. We can quote NFC modifications by trimethylsilylation (Lu et al. 2008), ring opening polymerization of poly(ε-caprolactone) (Lonnberg et al. 2011), cerium induced grafting (Stenstad et al. 2008), surface acetylation (Jonoobi et al. 2010; Tingaut et al. 2010), carboxymethylation (Eyholzer et al. 2010) or carbanilation (Siqueira et al. 2010b; Siqueira et al. 2009).

To the best of our knowledge, none of these papers studied the superficial and the internal degrees of substitution and they did not show the influence of molar ratio on the organization of the grafted agent at NFC surface. Indeed the target of our work is to determine and understand the effect of the molar ratio on the final properties of grafted moieties on NFC. Only Berlioz et al. (Berlioz et al. 2009) dealt with similar surface *vs*. internal organization but this work is different in terms of grafting conditions (gas esterification), characterization techniques (bulk analyses : XRD and CP-MAS NMR) and the investigated raw materials (nanocrystals and bacterial cellulose aggregated by freeze-drying). Moreover, in our study, using XPS and FE-SEM gives rise to a “real” surface scrutiny (XPS) with high resolution (FE-SEM). NFC final properties like thermal properties (TGA) or surface and rheological properties (contact angle and rheology) have also been studied, in this work. So, in comparison to the previous study in our group (Siqueira et al. 2010b), in which only one ratio have been tested, different stoichiometric ratios ([coupling agent]/[superficial OH functions]) have been investigated in the present work and the influence of degree of surface substitution has been discussed in detail in order to explain final properties of resulting grafted NFC. A special focus on aliphatic chain organization at the surface is proposed thanks to deeper X-Ray diffraction analyses.

1.2 Experimental

1.2.1 Materials

Native eucalyptus fibers used in this work were obtained from FIBRIA (Sao Paolo, Brazil). The coupling agent (n-octadecyl isocyanate), as well as the solvents (ethanol, acetone, toluene and dichloromethane) and the catalyst (IUPAC name: dibutyl(dodecanoyloxy)stannyl dodecanoate, common name: dibutyltin dilaurate), were purchased from Aldrich Co (FRANCE). All chemicals were reagent grade and used as received without further purification. Deionized water was used in all experiments.

1.2.2 Preparation of nanofibrillated cellulose (NFC)

Nanofibrillated cellulose suspension was produced from eucalyptus sulphite wood pulp after enzymatic pre-treatment (Endoglucanase Novozym® 476 supplied by Novozymes, Denmark, 0.1M, 2h, 50°C). Endoglucanase was chosen regarding their ability to cut macromolecular cellulose chains at their extremity and not in the middle of the chain. A suspension of bleached eucalyptus fibers (2.0% w/v) was disintegrated using a microfluidizer apparatus, Model M-110 EH-30. The slurry was injected through the Z-shape chamber of the apparatus under a high pressure. The Interaction Chamber (IXC) hosted cells of different sizes (400, 200 and 100µm). The fibers suspension was passed 3, 4 and 5 times in the Chamber fibrillation containing the three mentioned above different cells, respectively. Solid content of the treated suspensions was around 2% (w/w).

1.2.3 Chemical surface modification of NFC

Carbanilation reactions were performed following the reaction conditions developed by Siqueira et al. (Siqueira et al. 2010b). The temperature was changed in our case. The aqueous suspension (150g of suspension at 2%wt. which correspond to 3g of dried NFC), was first solvent exchanged from water to acetone by several successive centrifugations and re-dispersion operations. Centrifugation operations were conducted at 10,000rpm for 10min and re-dispersion steps, performed with high shear rate (Ultra-Turrax GT18) at 9,500-13,500rpm for 15s. Exchange solvent was performed in 4 successive steps.

The resulting acetone-based suspension was added in a three-necked round-bottomed flask of 250mL, equipped with a reflux condenser. The system was kept under dynamic flow of N_2 during the whole reaction time. The reaction mixture was heated to 65°C, in order to remove acetone. At the same time, 186mL of toluene is added dropwise to perform the *in situ* solvent exchange by removing slowly acetone and introducing toluene. At the end of toluene addition, 1mL of n-butyltindilaurate, as a catalyst (1mL) was added to the reaction medium. The temperature of the reaction mixture was then increased to 105°C and thermo-

stated using a contact thermometer. The temperature of system was kept at 105°C, for 2 hours after the isocyanate addition..

The quantity of octadecyl isocyanate has been calculated as equivalents with respect to the fraction of hydroxyl groups available at the surface of cellulosic nanofibers. For this study, it has been considered that only 4% of hydroxyl groups were available at the surface due to some calculations established by Siqueira et al. (Siqueira et al. 2010b) with similar dimensions of NFC. Such assumptions have been proposed to determine the surface hydroxyl group content because modeling of flexible heterogeneous nanofibrils is still under investigation. Some recent work, (Majoinen et al. 2011), have proposed an estimation of the amount of hydroxyl group present at the surface on cellulose nanocrystals which are more homogeneous and calibrated system.

After cooling at room temperature, the toluene suspension of modified NFC was then filtered and washed with dichloromethane (3 x 100mL) and with ethanol (3 x 100mL) under vacuum, in order to remove the formed by-products during the reaction (amines / urethanes), the unreacted physically adsorbed molecules and the excess of isocyanate (when needed). Moreover, a soxhlet extraction was performed for 24h using a mixture ethanol / dichloromethane with a ratio 1/1 (v/v) to complete the purification of modified NFC. Each reaction with different molar ratio has been triplicated.

1.2.4 Native and modified NFC Characterization

Scanning Electron Microscopy (FE-SEM)

A scanning electron microscope equipped with a field emission gun (FE-SEM), model Zeiss Ultra column 55 Gemini, was used to observe NFC. The accelerating voltage (EHT) was 3kV for a working distance of 6.4mm. A droplet of diluted suspension was then deposited onto a substrate covered with carbon tape. After drying, samples were coated with a 2nm layer of Au/Pd (Gold/Palladium) to ensure their conductivity. Sample preparations were at least duplicated and a minimum of 10 images by samples were observed with digital image analysis (Image J) for calculating dimensions. FE-SEM images selected in figures are representative to the sample.

X-Ray Diffraction (XRD)

The (wide angle) X-Ray Diffraction analysis was performed on powder obtained with air-dried neat NFC suspensions kept at ambient temperature (23°C) and relative humidity (28.8%). The grafted samples are obtained by casting and the ensuing films flakes were milled to produce powder. The samples were placed in a 2.5mm deep cell and measurements were performed with a PANanalytical, X'Pert PRO MPD diffractometer equipped with an X'celerator detector. The operating conditions of the refractometer were:

Copper Kα radiation (1.5418Å), 2θ (Bragg angle) between 5 and 60°, step size 0.067°, counting time 90s. The degree of crystallinity was evaluated using the Buschle-Diller and Zeronian Equation (Buschle-Diller and Zeronian 1992) :

$$I_c = 1 - \frac{I_1}{I_2} \qquad \text{Eq. 1}$$

Where: I_1 is the intensity at the minimum (2θ = 18°) and I_2 is the intensity associated with the crystalline region of cellulose (2θ = 22.5°). All measurements were made at least in duplicates and averaged.

Infrared spectroscopy (FTIR-ATR)

Infrared spectra were recorded, on film for unmodified NFC and powder form for modified NFC, using a Mattson 5000 spectrometer. The sample under investigation was deposited and pressed against the ZnSe crystal of an attenuated total reflectance (ATR) spectrophotometer. The torque applied was kept constant to ensure a same pressure on each sample. All spectra were recorded between 4000 and 700cm^{-1}, with a resolution of 4cm^{-1} and 16 scans. For each sample, a minimum of 2 spectra were obtained on different area of the film or the powder..

Elemental analysis (E.A)

Elemental analysis was carried out by the “Service Central d’Analyse (Vernaison, France)” of the “Centre National de la Recherche Scientifique” (CNRS). Carbon, Hydrogen, Nitrogen and Oxygen contents were measured for unmodified NFC and modified NFC. The data collected has allowed determining the degree of substitution (DS) which is the number of grafted hydroxyl groups per anhydroglucose unit according to the following equation:

$$DS = \frac{72.07 - \%C \times 162.14}{295.51 \times \%C - 228.19} \qquad \text{Eq. 2}$$

Where: C is the relative carbon content in the sample and 72.07, 162.14, 295.51 and 228.19 correspond to the carbon mass of anhydroglucose unit, mass of anhydroglucose unit, mass of n-octadecyl isocyanate and carbon mass of n-octadecyl isocyanate respectively. The analyses were performed twice and average was used.

X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) experiments were carried out using an XR3E2 apparatus (Vacuum Generators, UK) equipped with monochromated Mg Kα X-ray source (1253.6eV) and operating at 15kV under a current of 20mA. Samples were placed in an ultra-high-vacuum chamber (10^{-8} mbar) with electron collection by a hemispherical analyzer at a 90° angle. Signal decomposition was determined using Spectrum NT, and the overall spectrum was shifted to ensure that the C-C/C-H contribution to the C_{1s} signal occurred at 285.0keV. Comparison of the elementary surface composition was performed using the following equation:

$$O/C = (I_1 / I_2) \times (S_2 / S_1) \quad \text{Eq. 3}$$

Where: I_i is the intensity of signal i (carbon, oxygen, or nitrogen) and S_i (S_C = 0.00170, S_O = 0.00477 and S_N = 0.00299) denotes the atomic sensitivity factor whose values were calculated from:

$$S_i = \frac{T_i \lambda_i \sigma_i}{4\pi} \quad \text{Eq. 4}$$

With: T_i, λ_i and σ_i being the transmission energy, the electron inelastic mean free path, and the photoionization cross section for the X-ray source, respectively. T_i depends on the atomic kinetic energy E_i^{kin} (eV) according to:

$$T_i = \frac{1}{(E_i^{kin})^{0.7}} \quad \text{Eq. 5}$$

With: E_C^{kin} = 966.6eV, E_O^{kin} = 722.6eV, and E_N^{kin} = 851.6eV. The Penn algorithm was used to calculate the electron inelastic mean free path λ (λ_C = 2.63nm, λ_O = 2.11nm, and λ_N = 2.39nm) and the values were taken from Scofield (Scofield 1976) (σ_C = 1, σ_O = 2.85, and σ_N = 1.77).

XPS was performed on the dried powder of modified eucalyptus nanofibers. The XPS analysis for unmodified NFC (reference sample) was performed on a dried film treated in the same condition, but in the absence of the grafting agent and submitted to the same extraction procedure.

Contact angle measurement

Contact angle measurements were carried out by depositing different water droplets at the surface of the studied substrates and recording the angles formed using an OCA dataphysics system equipped with a CCD camera. The contact angle and drop volume acquisition was realized during the first 60 seconds after deposition taking 4images/s. For unmodified NFC,

the measurement was performed on dried film and on pellets for modified NFC. All measurements were performed 7 times for each sample.

Thermo Gravimetric Analyses measurements

A Setaram 92-12 TGA was used. About 50 mg of the sample were placed in the sample pan and tested with a heating rate of 10 °C/min from ambient temperature to 700°C under nitrogen flow. Experiments were at least duplicated and averaged.

Rheology measurements

Rheological measurements of the neat and modified NFC suspension, re-dispersed in water using 3% of sodium dodecylsulfate (SDS), w/w with respect to the dried NFC, were carried out using a controlled stress rheometer (MCR 301, Anton Paar Physica, Austria), with a parallel plate fixture (diameter 25mm with gap of 1mm) at 25.0°C controlled via a Peltier system. A solvent trap was used to prevent solvent (water) evaporation. Flow curves were plotted from the corresponding transient tests (apparent viscosity, η (Pa.s), vs. time at constant shear rate, $\dot{\gamma}$ (s^{-1}) at different shear rates) in a wide range from 0.001 to $1s^{-1}$. Flow curves were made in duplicate at each tested storage time (600 s).

1.3 Results and Discussions

1.3.1 Morphology and structure of neat NFC and grafted NFC

As already mentioned, different pretreatments have been developed with enzymes (Pääkkö et al. 2007; Siqueira et al. 2010c; Syverud et al. 2011), or involving chemical reactions (Saito et al. 2007; Saito et al. 2006; Saito and Isogai 2004), in order to decrease the energy consumption of cellulose fiber disintegration process. This leads to the production of totally different kinds of NFC with different final properties, as described recently (Siqueira et al. 2010c). Therefore, it is very important to specify the NFC under the conditions used to isolate them, whenever one should deal with them. The results presented on this work have been obtained with an enzyme (cellulase) pretreated bleached eucalyptus fibers disintegrated in a microfludizer meaning that mainly OH groups are present at NFC surface. In fact, such treatment conditions do not induce any chemical change (such as oxidation) on the substrate surface. The XPS results detailed latter confirmed this assumption.

The diameter of nanofibrillated cellulose was determined by digital image analysis (*ImageJ*) of FE-SEM pictures, as presented in the Figure 1-1.

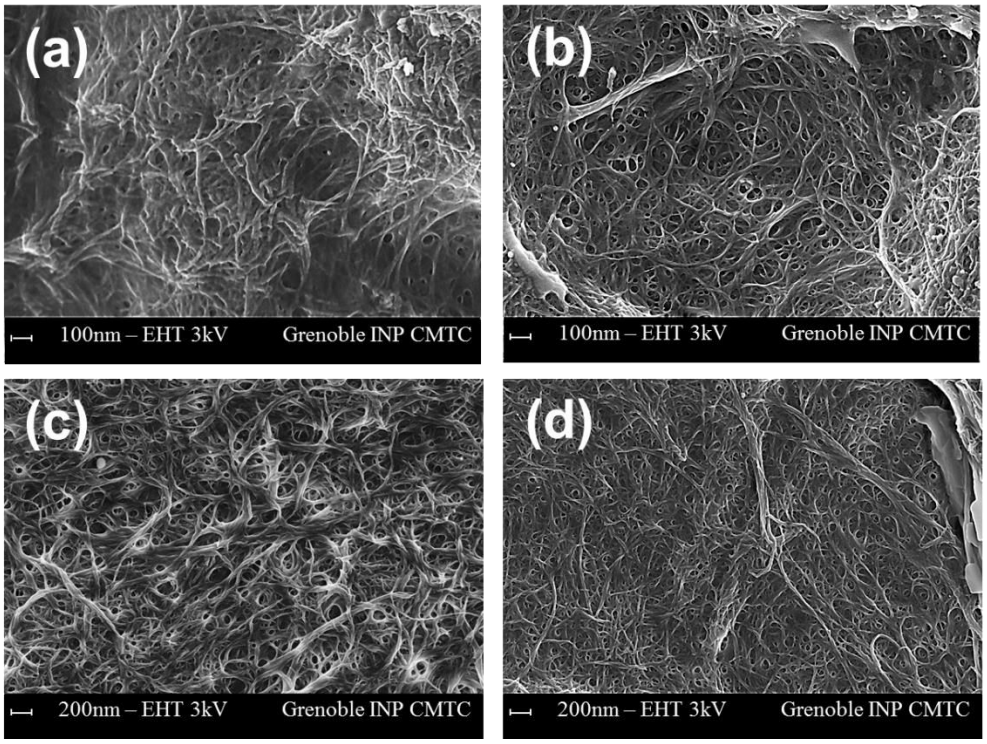


Figure 1-1 : FE-SEM pictures of (a) Neat NFC and modified NFC with the molar ratio (b) 1equiv, (c) 10 equiv and (d) 30equiv

The average diameter of neat NFC was about 22 ± 5nm (a minimum of 50 measurements was performed). The micrograph shows that nanofibrils are strongly entangled. After grafting, FE-SEM micrographs of NFC show similar average diameter 30 ± 8nm, 34 ± 9nm and 32 ± 7nm for the sample grafted with 1 molar equiv., 10equiv and 30equiv respectively. These figures have been confirmed by AFM as presented in Figure 1-2. Diameters gives 30nm, 32nm, 35nm for the samples grafted with 1, 10 and 30 molar equivalent respectively. It is worth to note that no morphology modifications are observed after grafting.

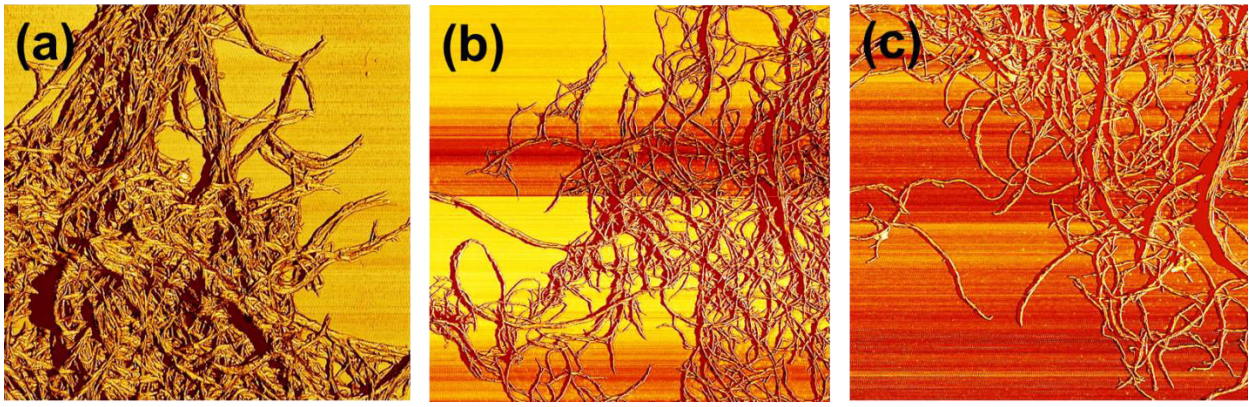
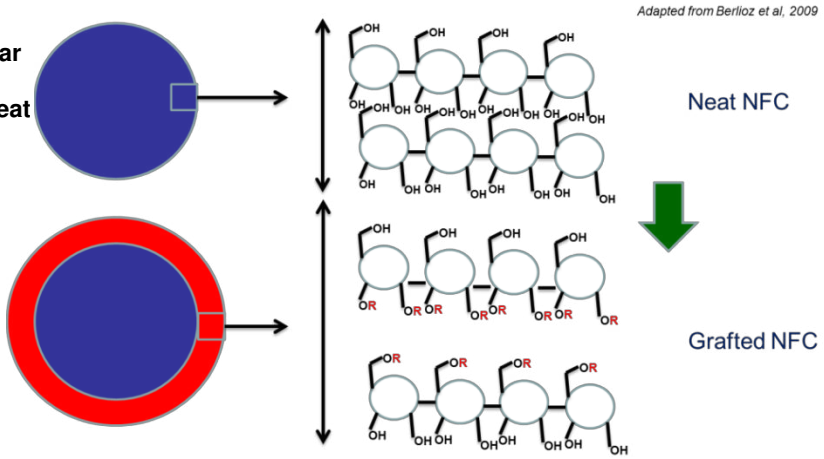


Figure 1-2 : AFM characterizations of grafted NFC with (a) 1equiv, (b) 10equiv and (c) 30equiv

According to XRD analyses (presented latter) the crystallinity index is similar for each samples. These two features confirm the relevance of non-swelling solvent used in our procedure. Moreover the “peeling effect” reported by Berlioz et al. (Berlioz et al. 2009) and Cetin et al (Çetin et al. 2009) on cellulose nanocrystals, is negligible in the case of nanofibrillated cellulose grafted with fatty chains. It is due to the length of the material (higher DP) which still contains appreciable amounts of hemicellulose and amorphous cellulose contrary to cellulose nanocrystals. Moreover the reaction by-products formed in our case (octadecanamine or dioctadecylurea), are less aggressive than HCl present in Berlioz’s study, which prevents the NFC from this swelling and peeling effect. Only surface grafting could occur and the size of the fatty chain (2nm) on the surface could explain the slight diameter increases. Moreover, the increasing of the diameter could also be induced by the increase of the distance between two cellulosic chains at the first surface layers as represented in the Scheme 1-1**.** In the native material, there is a well superposed and organized cellulosic chain packing. After the grafting, lower quantity of hydrogen bonds and some steric repulsion may occur between two cellulosic chains at the first surface layers increasing slightly the diameter of the NFC. Moreover, we can notice in Figure 1-1 that the grafted samples seem to yield less entangled NFC than that of neat counterpart due to limitation of hydrogen interaction, proving by the way the NFC grafting with obtention of

hydrophobic NFC. This is also simply proved by checking the NFC water suspensions homogeneity or the NFC films after drying, as shown in Figure 1-3.

Scheme 1-1 : Schematic representation of intramolecular interactions between two cellulosic chains comparing neat and grafted NFC



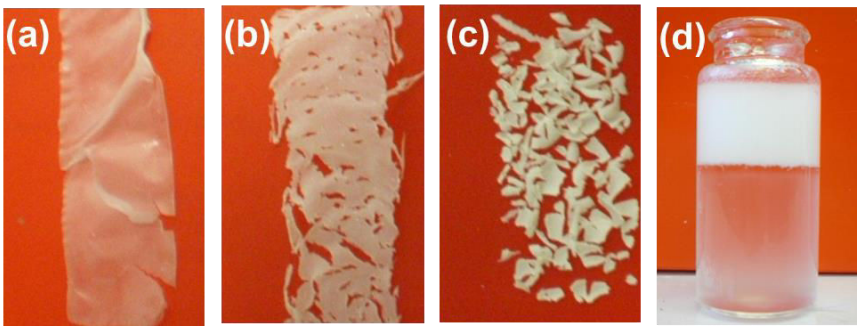


Figure 1-3 : Pictures of films obtained after casting of suspensions of (a) Neat NFC, NFC grafted with (b) 10equiv, (c) 30 equiv and (d) dispersion in water of NFC grafted with 10 equivalent

1.3.2 Efficiency of NFC grafting

FTIR spectroscopy was used to follow the efficiency of each grafting for the different reaction conditions. Figure 1-4 shows FTIR spectra obtained from: (a) neat NFC and NFC grafted using: (b) 1 molar equivalence; (c) 10 molar equivalences and (d) 30 molar equivalences of octadecyl isocyanate. Before the chemical treatment the cellulosic nano-fibers display several bands characteristic to cellulose macromolecules at 3350cm^{-1} (O–H), 1110cm^{-1} (C–O of secondary alcohol) (used for the normalization of all spectra) and 2868 and 2970cm^{-1} (C–H from –CH_2–). After reaction with the isocyanate, a characteristic band assigned to urethane bonding at 1735cm^{-1} has appeared. A substantial increase of the bands at 2868 and 2970cm^{-1} corresponding to asymmetric and symmetric –CH_2 – stretches from fatty chain was also observed. The peak associated with the vibration of adsorbed water at 1650 cm^{-1} strongly decreased after modification, probably because of the hydrophobic behavior of the modified material.

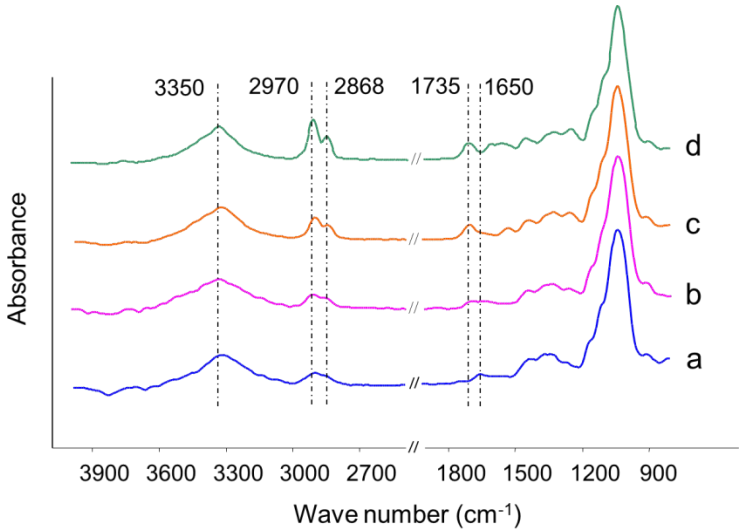
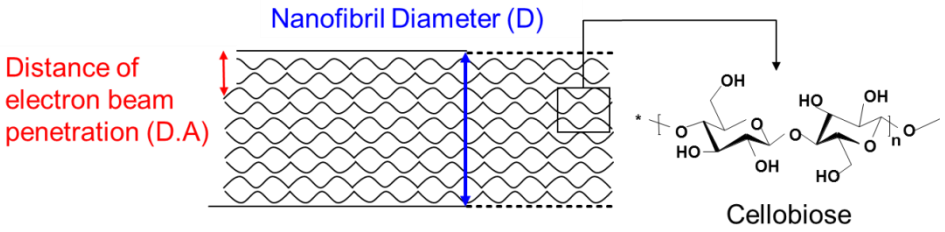


Figure 1-4 : Fourier Transform Infra-Red spectra of (a) neat NFC and grafted NDC with (b) 1equiv, (c) 10equiv and (d) 30equiv

Elemental Analyses (E.A) and X-ray Photoelectron Spectroscopy (XPS) were performed in order to quantify the grafting efficiency and to establish the degrees of substitution. Thus, E.A gives rise to the determination of the average degree of substitution (DS), whereas from XPS data the degree of substitution of the first nanometers layers (as shown in the Scheme 1-2) can be deduced. This parameter is also called degree of substitution of the surface (DSS) by some authors (Andresen et al. 2006; Goussé et al. 2002). The DS corresponds to the number of grafted hydroxyl function per anhydroglucose unit within the bulk of material and the DSS is linked to the number of grafted hydroxyl function per anhydroglucose unit present at the first surface layer (measurements carried out on about 7 nanometers). This depth of penetration and reliability of XPS has been established for planar surfaces. Surfaces with different roughness and different angular orientations to the beam may lead to different penetration profiles and results. However authors consider these 7 nanometers for their calculations and used it only for comparative study.



Scheme 1-2 : Schematic representation of cellulosic chain contained in one NFC with different parameters used for the calculation of the degree of substitution interne (DSI)

Both theoretical and experimental data obtained from the elemental weight composition for neat and grafted NFC are reported in the Table 1-1.

Theoretically, from anhydroglucose unit the weight ratio between oxygen and carbon atoms is 1.11, which corresponds to 49.4% and 44.4% for the elemental weight fraction of

oxygen and carbon, respectively. However, the experimental value of weight ratio (O/C) for neat NFC is 1.26 which gives 50.59 % of O and 40.38 % of C atoms. The difference could be explained by the presence of some O-rich impurities and by experimental errors (Labet et al. 2007). The presence of hemicelluloses (generally slightly richer in O atoms) in NFC suspension can also explain this difference.

Table 1-1 : Experimental and corrected elemental weight composition for neat and grafted NFC obtained by elemental analysis

Samples	Experimental values				Normalized Values	
	%C	%H	%N	%O	%C	%O
Neat NFC	40.38	6.19	<0.10	50.59	44.44	49.38
NFC 1 equiv	44.64	6.85	0.57	46.20	49.46	45.09
NFC 10 equiv	50.43	7.52	1.11	38.28	55.50	37.36
NFC 30 equiv	54.16	8.47	1.77	33.65	59.61	32.85

Surface layer composition of neat NFC and grafted samples at different molar ratio 1, 10 and 30 equivalences have been compared by XPS. The use of XPS to ascertain the efficiency of grafting was practiced very extensively the last decade and showed to be a very powerful technique to detect various changes at the surface. The XPS wide spectra (not shown) of the four samples show that in all cases the main peaks are detected at 285 and 532eV, corresponding to C and O atoms, respectively. These spectra show also the appearance of a new peak at 398eV, attributed to N atoms, whose concentration at the surface of grafted samples increases with increasing the stoichiometric ratio, as summarized in Table 1-2.

Qualitatively, two striking differences after grafting are noteworthy. On one hand, the characteristic signal at 285eV of C_{1S} increases with the grafting due to the evolution of the molar ratio with the presence of long aliphatic chain from the octadecyl carbamate. The ratio (O/C), reported in the Table 1-2, for all tested materials, decreased with the augmentation of the molar ratio. On the other hand, the signal of nitrogen appears at 405eV, which is also due to isocyanate moieties. Moreover based on these XPS results, an approximation of the grafted molecule density can be calculated (e.g. 0.4OH/nm² for 1equivalent). So the comparison to the OH density at the one surface layer (e.g. 0.2OH/nm² for 30nm of width for one NFC) clearly proves that the grafting occurs also at some internal macromolecules.

The first relevant works dealing with the use of X-ray Photoelectron spectroscopy to characterize cellulose substrates were reported by Gray's group (Dorris and Gray 1978a; Dorris and Gray 1978b; Gray 1978; Katz and Gray 1980). The deconvolution of C1s peak was reported by Ahmed et al. (Ahmed et al. 1987) showing that three entities are associated with carbon signal and centered at 285.0, 286.7 and 288.3eV. These moieties were attributed to C1 (C-H), C2 (C-O) and C3 (O-C-O and/or C=O), respectively. In theory (Belgacem and Gandini 2009), pure cellulose exhibits two peaks in its deconvoluted C_{1s} XPS spectra, namely (i) C-O at 286.7eV and associated to alcohols and ethers groups. This peak is noted as C2 and corresponds to 5 carbon atoms, and (ii) O-C-O at 288.3eV attributed to acetal moieties. This signal is noted C3 and corresponds to one carbon atom.

Table 1-2 : Mass concentration of each element for neat and grafted sample correlated to deconvolution C_{1S} obtained by XPS

Samples	Experimental values				Decomposition of C_{1s}					
	%C	%H	%N	O/C	C1(%)	C2(%)	C3(%)	C4(%)	C1/C3	C4/C3
Neat NFC	60.6	39.4	<0.1	0.65	15.1	67.8	16.8	0.4	0.90	0.02
NFC 1 equiv	63.8	34.8	1.1	0.55	20.6	52.1	22.9	5.8	0.82	0.28
NFC 10 equiv	67.9	29.9	1.8	0.44	35.8	43.0	15.1	6.1	2.4	0.40
NFC 30 equiv	82.0	14.9	3.1	0.18	63.4	24.7	7.7	3.3	8.6	0.32

In Figure 1-5, two additional peaks are observed for cellulose reference, namely: C1 and C4. As previously mentioned C1 signal corresponds to non-oxidized alkane-type carbon atoms associated with the presence of residual lignin, extractive substances and fatty acids. C4 peak was assigned to carboxylic functions originating from glucuronic acids borne by hemicelluloses (Johansson et al. 2004; Johansson et al. 2005) and present at the surface of lignocellulosic fibers and pulps destined to papermaking and used in our NFC production. In fact, such a raw material is generally known to contain up to 30% of this amorphous family.

In these works, it was also established that the surface O/C ratio for pure cellulose (theoretical formula) is 0.83. For the majority of virgin cellulose (avicel, wood pulps, annual plants, etc.), this ratio is systematically lower, because of the presence C-rich molecular segments at the surface of the solids under study. Table 1-2 confirms this assumption, in fact neat NFC presents a lower ratio O/C in comparison to theoretical value, i.e., 0.65 and 0.83, respectively. This difference could be attributed to the surface pollution by hydrocarbons adsorbed at the surface of nanofibers. Recently, Johansson et al, (Johansson et al. 2011)

proved also a possible adaptation of the NFC surface depending on the solvent used. Indeed Johansson et al. proved that depending on the solvent used with NFC, XPS analysis give strong difference. In this publication, DMA and toluene based NFC suspensions were dried and then analyzed using XPS. NFC dried from DMA present higher O/C ratio than those dried from toluene. After deconvolution only C2 and C3 peaks appear for DMA dried NFC contrary to toluene dried NFC where C1 and C4 are also present. Thus, this could also explain the difference obtained in our case.

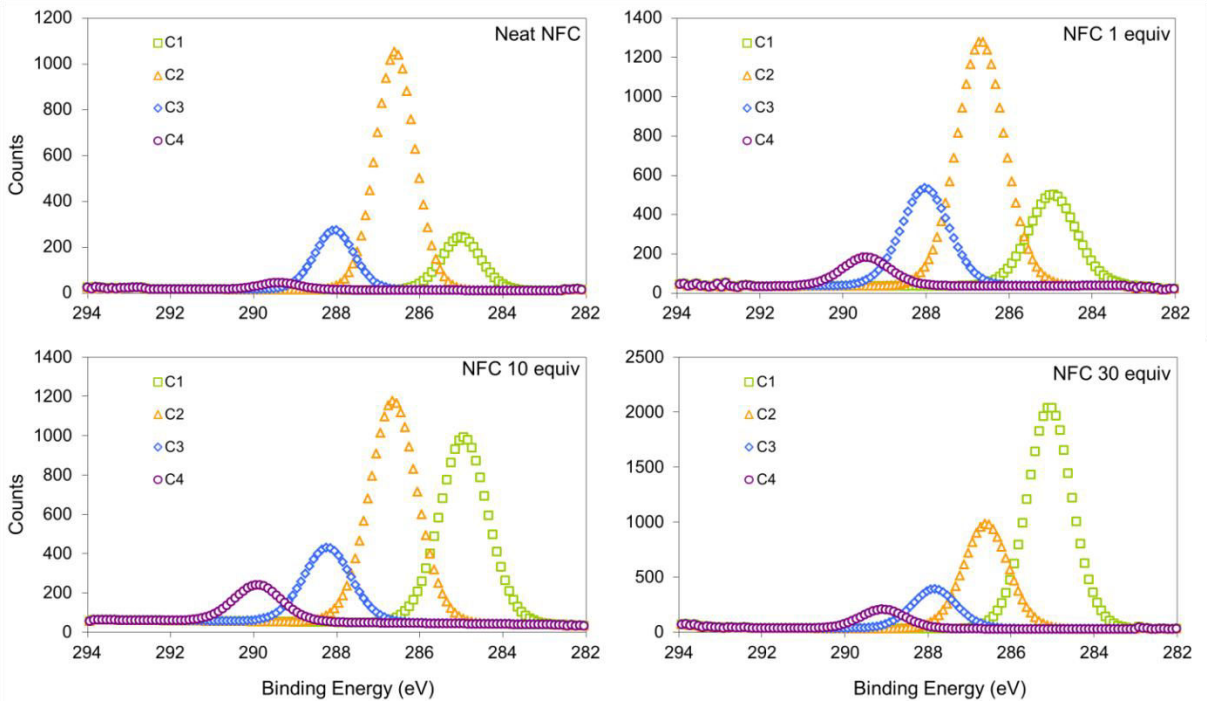


Figure 1-5 : Decomposition of the C1s signal into its constituent contribution for neat and grafted NFC as mentioned in the figure

A deconvolution of the signal C_{1S} presented in Figure 1-5, is required to quantify the grafting and corroborate the occurrence of surface grafting. This deconvolution reveals four peaks, which are attributed to C1 (C-H), C2 (C-O), C3 (O-C-O and/or C=O) and C4 (O-C=O), with a binding energy of 285.0, 286.6, 287.8 and 289.2eV, respectively, as summarized in the Table 1-2. This table shows that the intensity of C1 (C-C/C-H) increases strongly, from around 15 to 65%, for the virgin and highly grafted NFCs, respectively. Each glucose moiety possess *only* one C3-carbon, the ratio C1/C3 reflects the number of aliphatic carbons per glucose unit. The C1/C3 ratio shifted from 0.9 for neat NFC to 0.82, 2.40 and 8.60 for the NFC grafted with 1, 10 and 30 molar equivalence, respectively. This is the consequence of the strong impact of the C_{18} aliphatic chain. It is worth to note that the C1/C3 ratio for the lowest NFC grafting conditions (with 1 equivalent molar ratio) does not fit the increasing trend, probably because of low amounts of the coupled molecules. Similar analysis can be applied to C4/C3 ((O=C=O)/(O-C-O)) ratio which is also increasing with increasing the

stoichiometric ratios between the grafting molecules and the concentration of NFC superficial OH. The absolute values of C4 signals (link to the carbamate functions) increased with increasing the [NCO]/[OH] ratios. These results clearly evidence the occurrence of covalent bonding between the coupling molecules and cellulose surface.

Unfortunately, except technique like TOF-SIMS, it is quite difficult to know the composition of one surface layer. So XPS data could be used in order to determinate the DS of the surface (DSS) but taking into account the first surface layers. For the calculation of the DSS, several methods can be considered, but the most common is based on Goussé et al. work (Goussé et al. 2002), who defined the DSS (calculation done on the amount of nitrogen) as follow:

$$DSS = \frac{M_{AGU} \times x}{(100 \times M_N) - (M_{group\_grafted} \times x)} \qquad \text{Eq. 6}$$

where: M_{AGU} is the molar weight of one anhydroglucose unit (162.14g.mol^{-1}), M_N the molar weight of one atom of nitrogen (14g.mol^{-1}), $M_{group\_grafted}$ the molecular mass of the grafted moieties (295.51g.mol^{-1}) and x the mass concentration of nitrogen. Table 1-3 reports the DS values calculated from elemental analyses and the DSS determined using XPS. Another DS, called Degree of Substitution of Internal NFC (DSI), can then be calculated based on the idea that XPS correspond to around 7nm of depth of analysis. Combining elemental analyses and XPS data, the DS and the DSS can be used for the determination of this Internal Degree of Substitution (DSI). As mentioned before, this value could be very interesting to determine in order to assess the depth at which the grafting reaction took place. To the best of our knowledge, the following parameter is proposed for the first time:

$$DSI = \frac{N_{AGUtot} \times DS - N_{AGUsurf} \times DSS}{N_{AGUtot} - N_{AGUsurf}} \qquad \text{Eq. 7}$$

where: N_{AGUtot} is the total number of cellulose chains which contains the cross section of one nanofibril, $N_{AGUsurf}$ corresponds to the number of cellulose chains under scrutiny during the XPS measurements, as represented in the Scheme 1-2. The DS and the DSS are the degree of substitution calculated from elemental analysis and XPS measurements, respectively. N_{AGUtot} number was calculated as follow:

$$N_{AGUtot} = \frac{D}{W} \qquad \text{Eq. 8}$$

where: D is the mean diameter of NFC and W the width of one anhydroglucose unit (Hon and Shiraishi 2001) (0.5889nm). $N_{AGUsurf}$ is determined from the ratio:

$$N_{AGUsurf} = \frac{D.A \times 2}{W} \qquad \text{Eq. 9}$$

where: D.A is the XPS depth of analysis, 2 is used to take into account both edges of the nanofibers and W the width of one anhydroglucose unit.

Comparing the DS, DSS and DSI values, it seems that the grafting occurred mainly at the surface of the NFC for [NCO] / [OH] molar ratios of 1 and 30 equivalent samples, as summarized in Table 1-3. It was expected that DS is lower than DSS for all samples.

Table 1-3 : DS, DSS and DSI calculated from elemental analysis and XPS data

Samples	DS (E.A)	DSS (XPS)	DSI (XPS & E.A)
NFC 1 equiv	0.10	0.14	0.07
NFC 10 equiv	0.29	0.34	0.26
NFC 30 equiv	0.47	0.97	0.08

DS values are obtained from elemental analysis as previously discussed. It corresponds to a bulk analysis of all materials. DSS is obtained from XPS data and correspond to a surface characterization. Moreover, the condition for the grafting, as demonstrated before, was studied to be occurred only at the surface of NFCs. Also all grafts are located at the surface, which can explain the higher value of DSS in comparison to DS. Therefore, for the first molar ratio, since there is no excess of the grafting agent, the reaction is limited to the hydroxyl groups present at the surface of NFC substrate. Concerning the highest molar ratio (30 equivalent), the important amount of reagent introduced in the media may induce quick saturation of the hydroxyl groups present at the surface. The aliphatic chains grafted can also hinder the diffusion of other isocyanate moieties into the bulk of the materials, especially because the reaction is carried out in non-swelling conditions of solvent, pH and ionic force. That is why there is a higher DSS and a low DSI for this sample. However, the NFC sample, grafted using a molar ratio of 10, shows that deeper modification has occurred in the bulk of the nanofibrillated cellulose. This result is hard to rationalize but it does not constitute an experimental artifact. Indeed, this unexpected result was confirmed by repeating the experiment several times. An explanation is proposed in coming section.

So the DSI value seems to be a good way to check if the grafting is strictly performed at the surface. In some cases, the internal substitution is too small to induce a significant size change of the NFCs as observed previously. Even if this internal substitution could be also

attributed to highly substituted hemicelluloses and amorphous region of cellulose, the DSI seems very helpful to understand surface *vs*. internal grafting.

1.3.3 Organization of grafted aliphatic chain onto cellulose nanofibers and ensued properties of NFC

The crystalline structure of grafted NFC and neat NFC has also been investigated by XRD as shown in Figure 1-6. The crystalline structure of the cellulose is characterized by two main values of 2θ at 5.4Å (2θ = 18.5°) for the amorphous part and by a signal at 4,0Å (2θ = 22.5°) for the crystalline part. The degree of crystallinity is determined from equation 1, and values are 81.4, 77.7, 80.9 and 72.9 for respectively neat NFC, NFC grafted with 1, 10 and 30 equivalent. The reference sample presents a slightly higher degree of crystallinity (81.4) than the grafted ones. In fact, chemical surface modification induces a diminution of the crystalline part in cellulose as recently studied by Cetin et al (Çetin et al. 2009) on cellulose whiskers. Theoretically speaking, the higher is the amounts of grafts the lower degree is the crystallinity. In our work, the degree of crystallinity was found to be 77.7, 80.9 and 72.9 for the grafted samples with molar ratios of 1, 10 and 30 equivalents, respectively. The dropping of crystallinity index for the higher grafted sample is explained by the grafting of some crystalline part, so the quality of the crystals is altered.

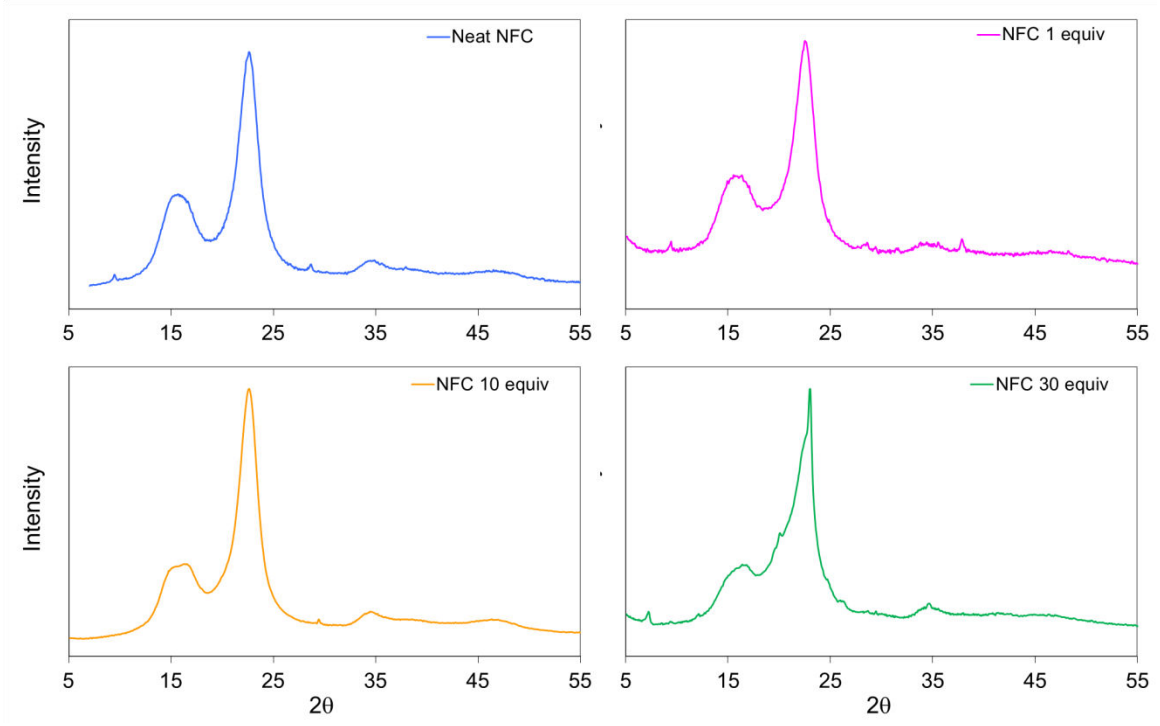


Figure 1-6 : X-Ray Diffraction patterns of neat NFC and the grafted samples as indicated in the figure

Moreover the XRD of the samples (Figure 1-6) display the presence of the peaks associated with the presence of cellulose but also a new narrow peak with rather weak

intensity at 12.12Å (2θ = 7.3°). This signal is assigned to the crystalline organization of the C_{18} aliphatic chain and it is generally identified as a second reflection order (Lee et al. 1997a). In fact, these phenomena were already observed and assigned to the local crystalline waxy domains organization of the aliphatic chain for a number of carbons higher than 7 (Huang et al. 2007; Menezes et al. 2009). This behavior is further confirmed by the presence of 2 other main peaks at 4.4Å (2θ = 20.4°) and 3.9Å (2θ = 23°) (Lee et al. 1997a), observed in Figure 1-6, for the NFCs with the highest grafting density (grafting with 30 equivalent molar ratio). These two peaks cannot be observed in the two others curves because of the lower grafting surface density of the corresponding samples. Even if, the last two peaks overlapped with those corresponding to cellulose, their shapes (a shoulder and a very sharp peak) can nevertheless be clearly noticed.

In order to confirm the proposed mechanism, an analysis at low angle was carried out. In fact, the first order reflection of the C18 aliphatic chain could be observed at 36.8Å (2θ = 2.4°) (Lee et al. 1997b) and can confirm local crystalline waxy domains structure at the surface of grafted cellulose nanofibrils. The results presented in the Figure 1-7 show a well-defined peak at 36.8Å (2θ = 2.4°).

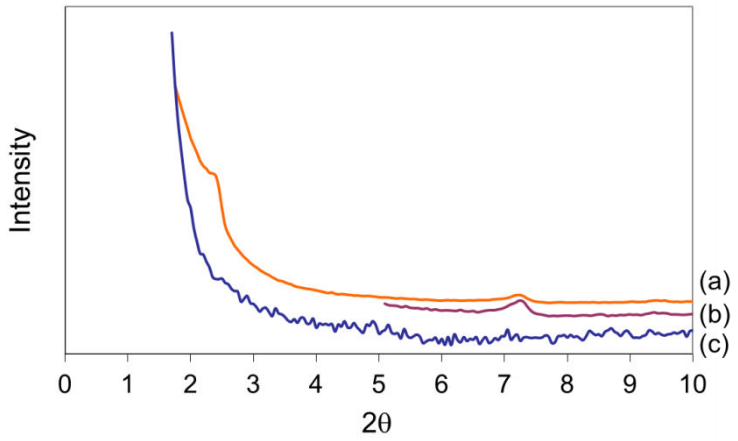
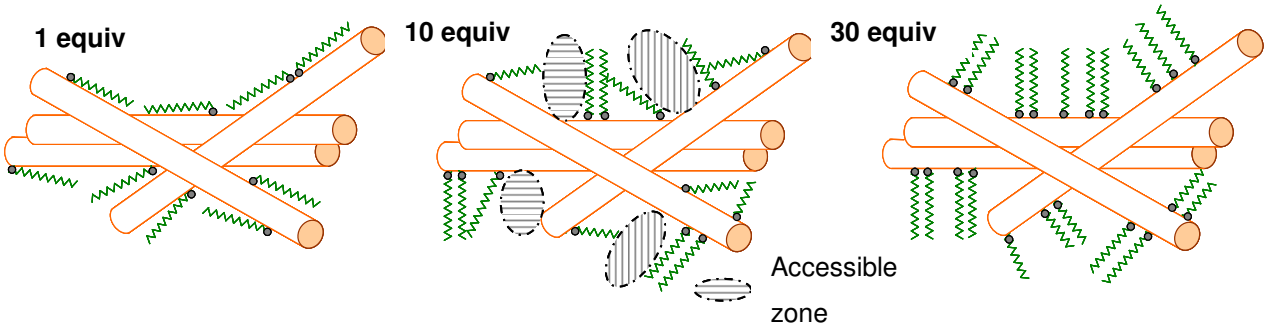


Figure 1-7 : X-Ray Diffraction patterns for NFC_30equiv at low angle (a), NFC_30equiv (b) and the substrate in platinum used for the analyses (c)

The presence of this shoulder is not due to a measurement artifact, since a substrate of platinum was also characterized and presented. Therefore, the obtained results strongly suggest that the grafted aliphatic chain at the surface of the NFC tend to form local crystalline waxy-like domains and helps to propose a surface organization of grafting in Scheme 1-3.

Indeed based on previous results (DSS and XRD) and NFC properties (described latter), the organization of the structure of the grafted layers could be represented as sketched in Scheme 1-3. This hypothesis allows explaining the crystallinity index evolution, the local crystalline domain structure and the different value of DSS. It is also a clear explanation for

the optimum of properties which will be presented in next chapter. Indeed some characterizations (e.g. contact angle and rheological measurement) were then performed in order to highlight this organization.



Scheme 1-3 : Schematic representation of the grafted NFC for the different ratio used for the chemical reaction as mentioned in the scheme

In addition, contact angle measurements were performed in order to point out the hydrophobic behavior of the grafted nanofibers comparing to neat NFC. The results are presented in the Figure 1-8. As expected the contact angle values of grafted NFC are higher than the neat NFC. Theoretically, the highest molar ratio corresponds to the highest contact angle value. However, the lowest contact angle value, around 80°, is observed for NFC grafted using 10 molar equivalences and the higher for NFC grafted in the condition 1 and 30 molar equivalence, around 90° respectively (+/- 2°).

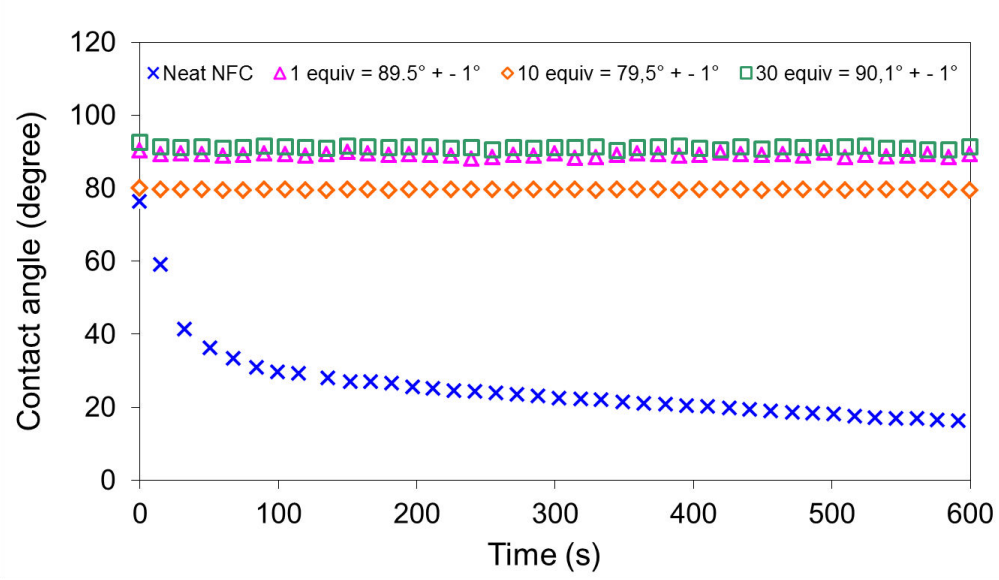


Figure 1-8 : Contact angle vs. time performed with water for (x) Neat NFC, (◊) NFC 10equiv, (Δ) NFC 1equiv and (□) NFC 30equiv

Even after several measurements, the same behavior is always observed. This might be due to the organization of fatty chain at the surface as previously detailed with Scheme 1-3.

Indeed the high amount of fatty chain can be organized as crystalline phase due to important Van der Waals interactions. In our case, organization at the surface can also be assessed by keeping in mind that the degree of substitution of surface (DSS) is increasing. In this case, linear increase of contact angle should be observed but it is not the case. This confirms our assumption and can be explained by the higher quantity of accessible zones at 10 equiv comparing to 1 equiv or 30 equiv grafted NFC, as proposed in Scheme 1-3.

Thermograms, obtained by TGA measurements and presented in Figure 1-9, show clearly similar impact of the grafting onto NFC surface. The grafted samples display an enhanced thermal resistance and so a lower sensitivity towards the degradation of the material in comparison to the neat NFC.

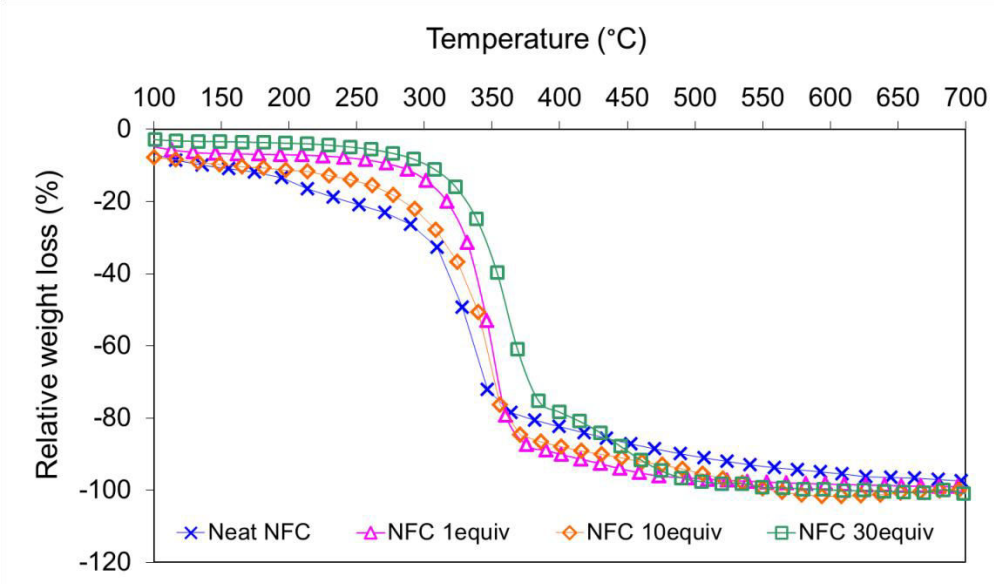
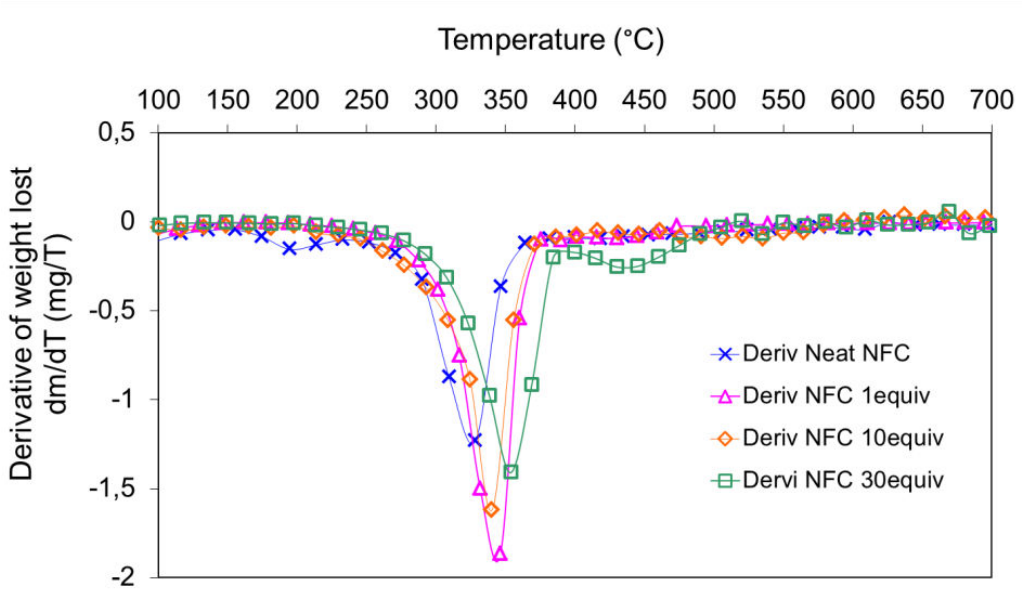


Figure 1-9 : TGA thermograph for (x) Neat, (◊) NFC 10equiv, (Δ) NFC 1equiv and (□) NFC 30equiv

The Figure 1-10 summarizes the temperature to reach a certain relative weight loss determined by the derivative of thermographs presented before. For instance at 241°C, the neat NFC lost 20% of weight. The same value is reached for higher temperature for the grafted sample, i.e. 317, 286, 331°C for 1equiv, 10equiv and 30equiv respectively. In this case the resistance to temperature is clearly highlighted by the ability of the grafts to be organized at the surface to protect NFCs. The sample grafted using a 10 times molar ratio displayed a lower value than other grafted samples. This behavior can be corroborated to the proposed organization in Scheme 1-3. Also authors supposed that local crystalline waxy domains can melt in order to act as a protective shell.



Samples	Relative weight loss (%) function of temperature(°C)						
	- 20%	- 30%	- 40%	- 50%	- 60%	- 70%	- 80%
Neat NFC	244	303	320	329	336	344	375
NFC 1 equiv	317	331	338	345	350	354	361
NFC 10 equiv	286	313	329	340	347	353	359
NFC 30 equiv	331	345	354	361	368	376	410

Figure 1-10 : Derivatives of thermograms for neat and grafted with 1 equiv, 10 equiv and 30 equiv. Table representing the weight lost associated to each sample

The performed rheological measurements point out the impact of grafting on viscosity properties of NFC suspensions. The water re-dispersed grafted samples (using as surfactant the sodium dodecyl sulfate, SDS) show a lower viscosity than neat NFC as shown in Figure 1-11. Two main assumptions can be proposed. The viscosity can decrease because of an aggregation effect of NFC in suspension inducing a loss of the nanoscale dimension. It seems that this is not the case, as confirmed by FE-SEM characterization. The second explanation is the lower number of hydrogen bonds between NFC as a result of the grafts which impedes such interactions. Figure 1-11 reveals the diminution of the viscosity for grafted samples. Moreover, the sample grafted with 10equiv has once again a different behavior with a higher viscosity than other modified substrates. It can be attributed to the “accessible zone” (presented in Scheme 1-3) which is not modified and still able to form hydrogen bond interactions.

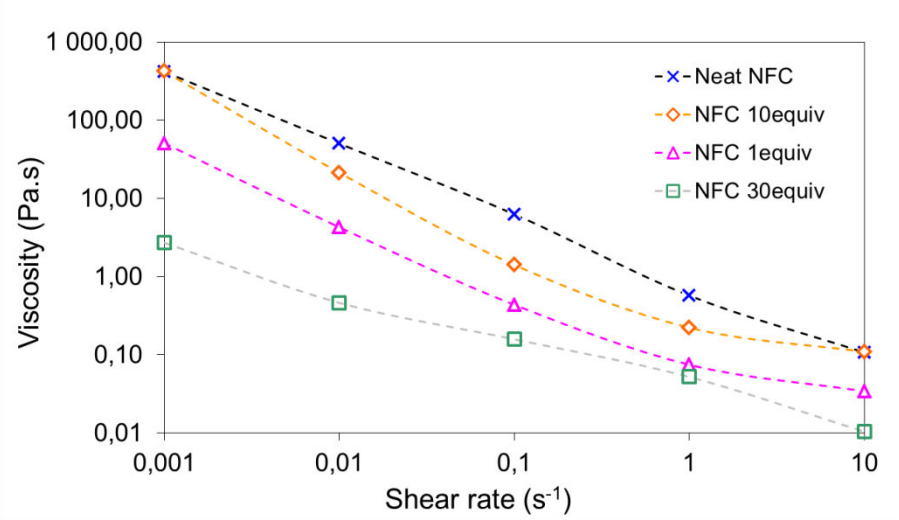


Figure 1-11 : Rheology measurement of neat NFC suspension and modified NFC after re-dispersion using SDS

Thanks to all characterizations, the proposed surface organization appears to be the correct explanation. It proves that a compromise in molar ratio is then necessary to achieve the best properties. Either very low or high grafting should be targeted in such NFC chemical modification process. That is the first time such compromise is proposed and proved.

1.4 Conclusions

This work shows that NFC substrate can be efficiently grafted by different molar ratio of fatty isocyanate and that the grafting density increases with increasing the molar ratio of the grafting agent. Moreover, thanks to XPS, an approach dealing with surface *vs*. bulk NFC chemical modification is proposed with definition of a new quantitative parameter (DSI). It helps discussing the grafted molecule organization at the NFC surface. Indeed, depending on the molar ratio, the grafted methylene groups tend to form local crystalline waxy-like domains resulting from lateral interaction between the aliphatic chains. Depending on the molar ratio, different surface organizations are assessed and proposed for the first time. Results of NFC physico-chemical properties confirmed the suggested organization. They proved that such surface organization monitor final NFC properties and that a compromise in molar ratio is then necessary to achieve the best properties.

Acknowledgment

This research was supported by the "Scale-Up of Nanoparticles in modern PAPermaking" (SUNPAP) project of the seven framework program of European research.

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2. Nanofibrillated cellulose surface modification in ionic liquid

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Abstract

The present study reports for the first time, the heterogeneous surface modification of nanofibrillated cellulose (NFC) in ionic liquid using different anhydride molecules. With ecofriendly perspectives in mind, the ionic liquid used was recycled by liquid–liquid extraction. The purity of the recycled IL was confirmed by FTIR measurements and NMR spectra of ^{1}H, ^{13}C, ^{31}P and ^{19}F. All the NFC samples were characterized by different techniques (e.g. FTIR, contact angle measurements) to check the efficiency of grafting and to compare the influence of the different anhydrides used. The surface chemical grafting obtained was effective. The Degree of Substitution (DS) was determined by elemental analysis and the Degree of Surface Substitution (DSS) was calculated from X-ray photoelectron spectroscopy data. ToF-SIMS was used to characterize the grafting at the extreme surface.

Keywords

Nanofibrillated Cellulose (NFC), Chemical surface modification, Ionic liquid, Anhydrides, ToF-SIMS

***Inspired from**: Karim Missoum, Naceur Belgacem, Julien Bras – Soft Matter (2012) – Accepted*

2.1 Introduction

Cellulose is the most abundant bio-based polymer (Belgacem and Gandini 2008) available in large amounts anywhere on earth. Its abundance, biodegradability, recyclability and renewability make cellulose one of the best alternative raw materials to oil-based sources. The last decade has been focused on obtaining efficient material from cellulose fibers with an exponential interest on nano-scaled cellulose-based elements. Several types of nanocellulose can be found in the literature: the cellulose nanocrystals (or whiskers) obtained by acid hydrolysis of cellulose and cellulose microfibrils or nanofibrils (NFC) obtained by mechanical treatments usually combined with enzymatic and/or chemical pre-treatment of cellulosic materials. Very recent reviews give detailed information for each material (Eichhorn et al. 2010; Habibi et al. 2010; Siró and Plackett 2010) and their application in bionanocomposite (Siqueira et al. 2010a) or as film or coating (Lavoine et al. 2011). The present study focuses on cellulose microfibrils (MFC, NFC) firstly obtained by Herrick et al. (Herrick et al. 1983) and Tubark et al. (Turbak et al. 1983) in 1983 using mechanical disintegration of wood pulp. The diameter of nanofibrils is in the range of 10 to 50 nm (Walther et al. 2011), whereas the typical length is several micrometers (Chinga-Carrasco and Syverud 2010). Different pre-treatments such as enzymatic (Pääkkö et al. 2007; Siqueira et al. 2010c; Siqueira et al. 2010d; Syverud et al. 2011) or TEMPO mediated process (Saito et al. 2007; Saito et al. 2006; Saito and Isogai 2004; Isogai et al. 2011), have nowadays been developed to obtain more homogeneous suspensions and to limit energy consumption. The obtained NFCs show improved properties (e.g. mechanical, barrier) and allow efficient bionanomaterials to be made.

Unfortunately, NFCs tend to form an aqueous gel at very low concentration (2% wt) due to their important specific surface area and consequently the high number of hydrogen bonds arising from surface hydroxyl groups. This feature is the main drawback of their use in several applications, such as coating formulations (low solid content and high viscosity). The aggregation or the film-forming capacity of NFCs in their dried form is another inconvenience, mainly for composite applications. To overcome these handicaps, different solutions are studied but the most developed is the surface chemical modification, transforming hydroxyl groups into other functions thus limiting (or even totally avoiding) the formation of hydrogen bonds.

Over the last two decades, many processes of cellulose fibers surface modification have been investigated, as recently reviewed by one of us (Belgacem and Gandini 2009; Belgacem and Gandini 2008; Gandini and Belgacem 2011). Nevertheless, only a few and

very recent works have been reported on the grafting of nanocellulose nanoparticles (whiskers or nanofibrillated cellulose).

Different techniques can be noticed for such NFC modifications as trimethylsilylation(Lu et al. 2008), ring opening polymerization of poly(ε-caprolactone) (Krouit et al. 2008), cerium induced grafting (Stenstad et al. 2008), surface acetylation(Jonoobi et al. 2010; Radionova et al. 2010; Tingaut et al. 2010), carboxymethylation (Eyholzer et al. 2010) or carbanilation (Siqueira et al. 2010b; Siqueira et al. 2009). To perform these reactions, large quantities of organic solvents as liquid media for chemical reaction, for extraction or in formulation are overused. In most cases, these dispersing organic media are hazardous to health, flammable and volatile. To limit the use of such organic solvents, a novel type of “green” solvents has been studied during these past decades, i.e.: the Ionic Liquids (ILs) (Earle and Seddon 2000; Olivier 1999).

Ionic liquids or “molten salts” are in general defined as liquid electrolytes composed entirely of ions. More recently(Baker et al. 2005; Hardacre 2007; Holbrey and Seddon 1999), the melting point criterion has been proposed to distinguish molten salts (“high melting point, high viscosity and corrosive medium”) and Ionic Liquids (“liquid below 100°C and low viscosity”). The most important features of ILs is their non-measurable vapor pressure. They are defined as “green” solvents mainly because of the absence of volatile organic compounds (VOC) emission. Also in term of inhalation and vapor of solvent, the risk is limited in comparison to other volatile organic solvent in spite of IL toxicity. Furthermore, ILs have other attractive properties, such as high chemical and thermal stability (Blake et al. 2006; Chiappe and Pieraccini 2005; Zhang et al. 2006), nonflammability, as well as high ionic conductivity. They could be also easily recyclable and reused due to their low melting point (comprising -60°C to +60°C), just by decreasing the temperature or by distillation. There is a wide variety of ILs, each of them is composed of a cation (e.g. imidazolium or pyridinium salts) and an anion (e.g. chloride, tetrafluoroborate, hexafluorophosphate…).

Ionics liquid are well known to unexpectedly solubilize different polymers (Erdmenger et al. 2010; Guerrero-Sanchez et al. 2011; Guerrero-Sanchez et al. 2008) and biopolymer. Moreover, chemistry and interactions between cellulose and ionic liquids have been investigated, mainly in the context of solubilization or homogeneous derivatization of cellulose (Biswas et al. 2006; Feng and Chen 2008; Swatloski et al. 2002). Indeed some ionic liquids are promising solvents for chemical reactions involving dissolved cellulose and different reactions have already been performed (Jain et al. 2005; Liebert and Heinze 2008) using acetyl chloride (Granström et al. 2008; Heinze et al. 2005), acetic anhydride(Abbott et al. 2005; Köhler et al. 2007; Vaher et al. 2002; Wu et al. 2004) and phenyl isocyanate

(Barthel and Heinze 2006; Schlufter et al. 2006). To limit this dissolution, a hydrophobic IL could be used and different parameters (i.e. viscosity, polarity, affinity with water and dissolution in water) must be considered (Freire et al. 2007; Rivera-Rubero and Baldelli 2004; Shvedene et al. 2005; Wong et al. 2002).

Several procedures have been developed to recycle ILs with an acceptable degree of purity. Liquid-liquid extraction or cooling precipitation has been used to remove impurities (Chapeaux et al. 2008; Dupont et al. 2002; Earle and Seddon 2000; Muthusamy and Gnanaprakasam 2005; Zhao et al. 2005). At the end of the reaction, modified materials could be easily removed by filtration and the formed impurities, by-products and unreacted reagents can be separated by liquid-liquid extraction or distillation.

In the present study, [bmim][PF_6] has been considered for the first time to perform the surface chemical modification of cellulose nanofibers. Indeed, the target of this paper is the esterification of NFC surface in heterogeneous conditions. Different anhydride molecules have been tested and their influence on the nanofiber morphology and the degree of substitution established. A special focus on recyclability / purification of the ionic liquid will also be proposed. To the best of our knowledge, there are no papers available in the literature dealing with the grafting of heterogeneous cellulose nanoparticles in ionic liquids. To ascertain the surface chemical grafting Time of Flight Secondary Ions Mass Spectroscopy (ToF-SIMS) was used. This technique was applied for the first time for the characterization of the chemical surface modification of nanofibrillated cellulose.

2.2 Experimental

2.2.1 Materials

The wood pulp delivered by Domsjö (Sweden) corresponds to a mix between Spruce and Pinus with a mass ratio of 70% and 30%, respectively. The reagents i.e., acetic, butyric, iso-butyric and hexanoic anhydride, the ionic liquid [bmim][PF6] and the other compounds used here (i.e., ethanol, acetone, dichloromethane, sodium hydroxide, ethyl ether) were purchased from Sigma-Aldrich and co. (France). All chemicals were reagent grade and used as received without further purification. Deionized water was used in all the experiments.

2.2.2 Nanofibrillated cellulose production (NFC)

Nanofibrillated cellulose suspension was produced by the FCBA institute (Grenoble, France), from a pre-treated bleached Domsjö wood pulp using an endo-glucanase (cellulase) enzyme, during 2h at 50°C, A suspension of bleached Domsjö fibers (2.0% w/v) was pumped through a microfluidizer processor, Model M-110 EH-30. The slurry was pushed into Interaction Chamber (IXC) using cellules of different sizes (400, 200 and 100 µm), under a high pressure, thus producing the size reduction of the initial fibers. The fibers suspension was recirculated 3, 4 and 5 times through 400, 200 and 100µm cellules in the fibrillation chamber, respectively. The weight yield of this disintegration operation is higher than 95% and the solid content of the suspension is around 2% (w/w).

The starting raw material is bisulfite pulps and its hemicelluloses content is very low (less than 3.5% w/w). We have, therefore, neglected them. Anyway, they have very similar structure (OH-rich macromolecules).

2.2.3 Chemical surface modification of NFC in IL

The aqueous suspension of NFC (~ 2%wt), was solvent exchanged from water to acetone by several successive centrifugations and re-dispersion operations. Centrifugation steps were conducted at 10,000rpm for 10min and re-dispersion steps performed with high shear rate tool (Ultra-Turrax GT18) used at 9,500-13,500rpm for 15s. Solvent exchange was performed in 4 successive steps. The water content, in the suspension, was determined and found to be less than 1%wt. The solvent exchange limits presence of water in NFC, as confirmed by FTIR (not shown).

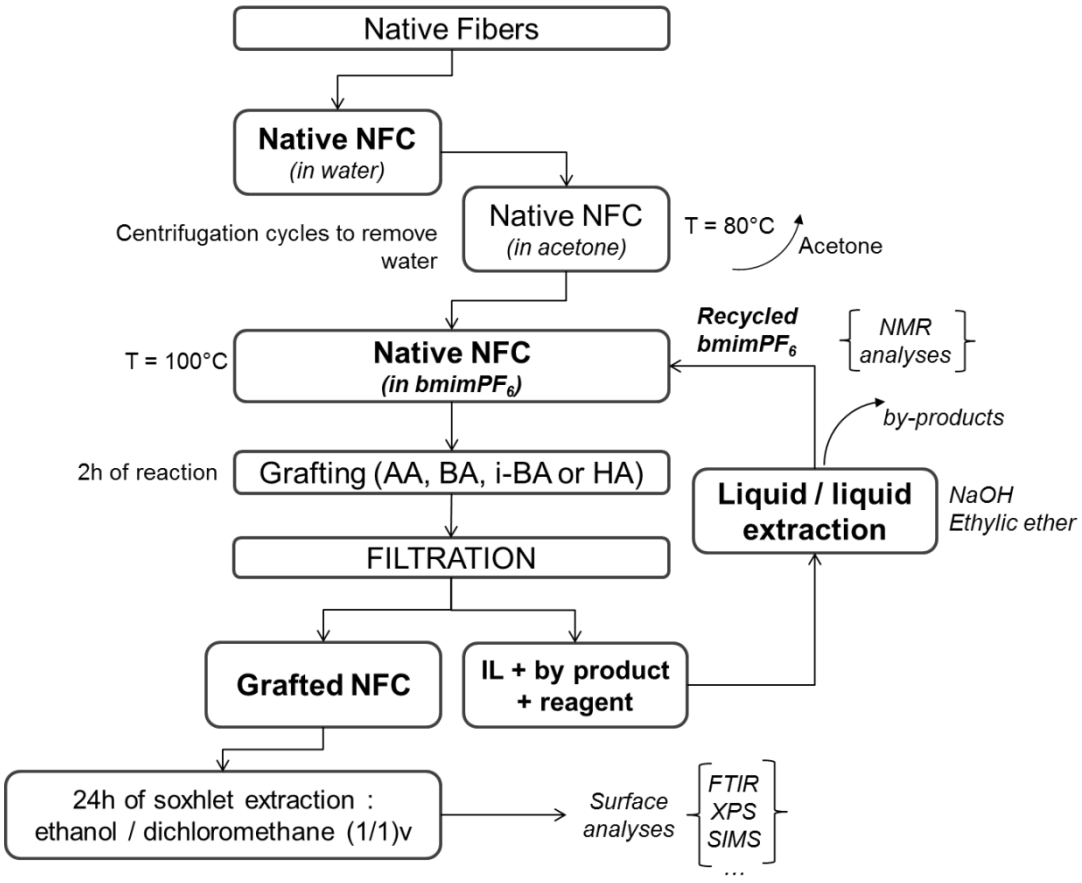
Then the suspension containing 3g (dry weight) of nanofibrillated cellulose dispersed in acetone was transferred into a three-necked round-bottomed flask of 250mL, equipped with a reflux condenser. The ionic liquid (120g of [bmim][PF6]) was added and the reaction

mixture was heated to 80°C, in order to remove acetone. This *in-situ* solvent exchange for NFC has already been proposed and commented in a previous paper (Siqueira et al. 2010b).

All anhydride quantities have been calculated, with respect to the hydroxyl groups available at the surface of cellulosic nanofibers. For this study, it has been considered as rough estimation that only 4% of hydroxyl groups were available at the surface, as already established in a previous paper (Siqueira et al. 2010b). Thus, in this work 10 folds equivalent molar have been added. The temperature of system was kept for 2 hours at 100°C after anhydride addition. After cooling at room temperature, the suspension of modified NFC was then filtered and washed with dichloromethane (3 x 100mL) and with ethanol (3 x 100mL) using a vacuum flask to remove the released carboxylic acid elimination product, the ionic liquid and the excess of the used anhydride. A soxhlet extraction was performed for 24h using a mixture ethanol / dichloromethane with a ratio 1/1 (v/v) to achieve the purification at 80°C. All extractants have been verified to be miscible and soluble in this mixture of organic solvents.

2.2.4 Ionic Liquid recycling

A liquid-liquid extraction was used for the recycling of the IL. Thus, two cycles of washing using approximately 250mL of 0.1M sodium hydroxide solution were performed to remove the formed by product and the unreacted reagents. This procedure was followed by a further purification step using two cycles of extraction with di-ethylether (150mL per cycle) and repeated twice, as presented in the Scheme 2-1. The ionic liquid being one phase by itself.



Scheme 2-1 : Procedure for grafting and recycling

2.2.5 Characterizations tools

Scanning Electron Microscopy (FE-SEM)

A scanning electron microscope equipped with a field emission gun (FE-SEM), model Zeiss Ultra column 55 Gemini, was used to observe the NFC particles. The accelerating voltage (EHT) was 3 kV for a working distance of 6.4 mm. A droplet of diluted suspension, in acetone for modified samples and water for neat NFC, was deposited onto a substrate covered with carbon tape and coated with a 2 nm layer of Au/Pd (Gold/Palladium) to ensure the conductivity of all samples.

X-Ray Diffraction (XRD)

The (wide angle) X-Ray Diffraction analysis was performed on NFC films obtained after air-drying of neat NFC suspensions kept at ambient temperature (23°C) and relative humidity (28,8%). The grafted samples are obtained by casting and ground in powder form. The samples were placed in a 2,5mm deep cell and the measurements were performed with a PANanalytical, X'Pert PRO MPD diffractometer equipped with an X'celerator detector. The operating conditions for the refractometer were: Copper Kα radiation (1.5418 Å), 2θ (Bragg

angle) between 5 and 60°, step size 0,067° and counting time 90s. The degree of crystallinity was evaluated using the Buschle-Diller and Zeronian (Buschle-Diller and Zeronian 1992) Equation:

$$I_c = 1 - \frac{I_1}{I_2} \quad \text{Eq. 1}$$

where I_1 is the intensity at the minimum (2θ = 18°) and I_2 is the intensity associated with the crystalline region of cellulose (2θ = 22.5°). All measurements were made at least in duplicates.

Infrared spectroscopy (FTIR-ATR)

Infrared spectra were recorded, on film for unmodified NFC and powder for modified NFC, using a Perkin-Elmer SP100 spectrometer. For each sample, the Diamond crystal of an attenuate total reflectance (ATR) apparatus was used. The torque applied was kept constant to ensure the same pressure on each sample. All spectra were recorded between 4000 and 700 cm^{-1}, with a resolution of 4cm^{-1} and using 8 scans. A minimum of 2 spectra were obtained on different area of the film or the powder for each sample.

Contact angle measurement

Contact angle measurements were carried out by depositing different water droplets at the surface of the studied substrates and recording the angles formed using an OCA dataphysics system equipped with a CCD camera. The contact angle and the drop volume acquisition were realized during the first 60 seconds after deposition taking 4images/s. For unmodified NFC, the measurement was performed on dried film and on pellets for modified NFC. All measurements were performed 7 times for each sample.

Elemental analysis (E.A)

Elemental analysis was carried out by the “Service Central d’Analyse (Vernaison, France)” of the “Centre National de la Recherche Scientifique (CNRS)”. Carbon, Hydrogen, Nitrogen and Oxygen contents were measured for unmodified NFC and modified NFC. The collected data has allowed the degree of substitution (DS) to be determined which is the number of grafted hydroxyl groups per anhydroglucose unit according to the following equation:

$$DS = \frac{6 \times Mc \; - \; \%C \times M_{AGU}}{M_{estergrafted} \times \%C \; - \; M_{Cestergrafed}} \quad \text{Eq. 2}$$

where %C is the relative carbon content in the sample and Mc, M_{AGU}, $M_{estergrafted}$ and $M_{Cestergrafted}$ correspond to the carbon molecular mass of anhydroglucose unit, the molecular mass of anhydroglucose unit, the mass of the grafted ester and the carbon mass of the grafted moieties respectively. The analyses were performed twice and the average was used.

X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) experiments were carried out using a Kratos Axis Ultra DLD apparatus (Vacuum Generators, UK) equipped with an unmonochromated Aluminum Kα X-ray source (1486.6 eV) and operating at 15 kV under a current of 8 mA. Samples were placed in an ultra-high-vacuum chamber (10^{-8} mbar) with electron collection by a hemispherical analyzer at a 90° angle. Signal decomposition was determined using Vision 2.2.8 software, and the overall spectrum was shifted to ensure that the C-C/C-H contribution to the C 1s signal occurred at 284.6 eV.

XPS was performed on the dried powder of modified NFC nanofibers. The XPS analysis for neat NFC was performed on a dried film treated in the same condition, extracted but ungrafted. For the calculation of the degree of substitution of the surface several methods can be considered. The most common is based on Andresen et al. (Andresen et al. 2006) who defined the DSS (calculation done on carbon presence of C1 and C3 carbon intensity) as follow:

$$DSS = \frac{-\%C4 \times M_{AGU}}{\%C4 \times M_{grafts} - Mc} \qquad \text{Eq. 3}$$

Where: %C4 is the intensity of the signal attributed to O-C=O moieties, M_{AGU} the molecular mass of an anhydroglucose unit (162.14g.mol^{-1}), M_{grafts} the molecular weight of the grafted moieties (42.038, 70.092 and 98.066g.mol^{-1} for acetate, butyrate and hexanoate functions) and Mc the molecular weight of one carbon atom.

Nuclear Magnetic Resonance (NMR)

NMR experiments were conducted at 25°C in DMSO-d6 99.8% (Aldrich) on a UNITY Varian spectrometer, equipped with a 5 mm id-pfg probe (indirect detection-pulse field gradient) operating at 399.959MHz, 376.308MHz and 161.889MHz for ^{1}H, ^{19}F and ^{31}P respectively. For ^{13}C spectra, a 10mm BB probe (broad band) operating at 100.580MHz was used. NMR spectra of pristine and recovered product are recorded with similar conditions.

The quantitative ^{1}H-NMR spectra were performed at 25°C. The one-pulse sequence was used with a 30° pulse, a relaxation delay of 60s, a spectral width of 4500Hz and 16K data points for acquisition. Zero-filling was carried out without apodization. The positions of the peaks were referred to the residual solvent peak DMSO-d6 (δ = 2.49ppm). Chemical shifts are given relative to tetramethylsilane.

^{19}F chemical shifts are given with respect to $CFCl_3$ (δ = 0ppm). ^{19}F-NMR spectra were acquired using a 11300Hz spectral width, 64K data points, 2.8s acquisition time, 10s relaxation delay and 45° pulse. In this case, there was no proton decoupling. Zero-filling was carried out without apodization.

^{31}P chemical shifts are given with respect to H_3PO_4 (δ = 0ppm). The spectra were acquired using 30000Hz spectral width, 64K data points, 1s acquisition time, 5 s relaxation delay and 30° pulse. There was no proton decoupling. Zero-filling was carried out without apodization.

^{13}C-NMR chemical shifts are given with respect to tetramethylsilane. The positions of the peaks were referenced using the residual solvent peak of DMSO-d6 (δ = 39.50ppm). Quantitative spectra (proton broad band decoupling only during acquisition time) were obtained with a 25000Hz spectral width, 32K data points, 0.64s acquisition time, 45s relaxation delay, and 30° pulse. Zero-filling and 4Hz line broadening are applied before FT (Fourier transform).

Time-of-Flight Secondary Ions Mass Spectrometry (ToF-SIMS)

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) depth profiling was performed with a TOF SIMS V tool from ION-TOF GmbH with a bismuth liquid-metal ion source for analysis, incident at approximately 45° with respect to the sample. The surface spectra were acquired by analysis of both positive and negative secondary ions in separate acquisitions. For the analysis, a 25 keV Bi^+ or Bi_3^+ beam was used with a 500 µm × 500 µm raster in order to average over a large sample area. Vacuum in the analysis chamber was kept between 7×10^{-8} Pa and 1×10^{-7} Pa, while profiling, in order to reduce the influence of residual gases (typically oxygen and hydrogen).

2.3 Results and discussions

2.3.1 Morphological and structural properties

The chemical surface modification of NFC has been achieved for the first time in ionic liquid ($BmimPF_6$) with several anhydrides, as described in Scheme 2-1. As already mentioned (Siqueira et al. 2010d), it is very useful to specify the conditions used to isolate NFC. This study used NFC obtained with enzyme pretreated bleached wood fibers disintegrated in a microfludizer. Such treatment conditions do not induce any chemical change (such as oxidation) on the substrate surface and consequently, the groups present at NFC surface are mainly OH functions. The XPS results given afterwards confirmed this assumption.

The diameter of nanofibrillated cellulose was determined by digital image analysis (*ImageJ*) of FE-SEM pictures, as presented in Figure 2-1.

The average diameter of neat NFCs was about 20 ± 5nm (a minimum of 50 measurements was performed). The micrograph shows that neat NFCs are strongly entangled. Whereas the network of grafted NFCs is more porous, showing already less hydrogen bond interactions between grafted NFC.

The FE-SEM micrographs indicate that the morphology and the nanoscale of NFCs are conserved after grafting confirming the relevance of the ionic liquid selected as a non-swelling solvent. FE-SEM micrographs show also a slight increase of the average diameter with as a function of the length of the aliphatic chain grafted: 36 ± 12nm, 40± 16nm, 55 ± 18nm and 54 ± 15nm, for the sample grafted with acetic, butyric, iso-butyric and hexanoic anhydride respectively. However the standard deviation is quite high, which limits the interpretations, even if a certain trend could be noticed.

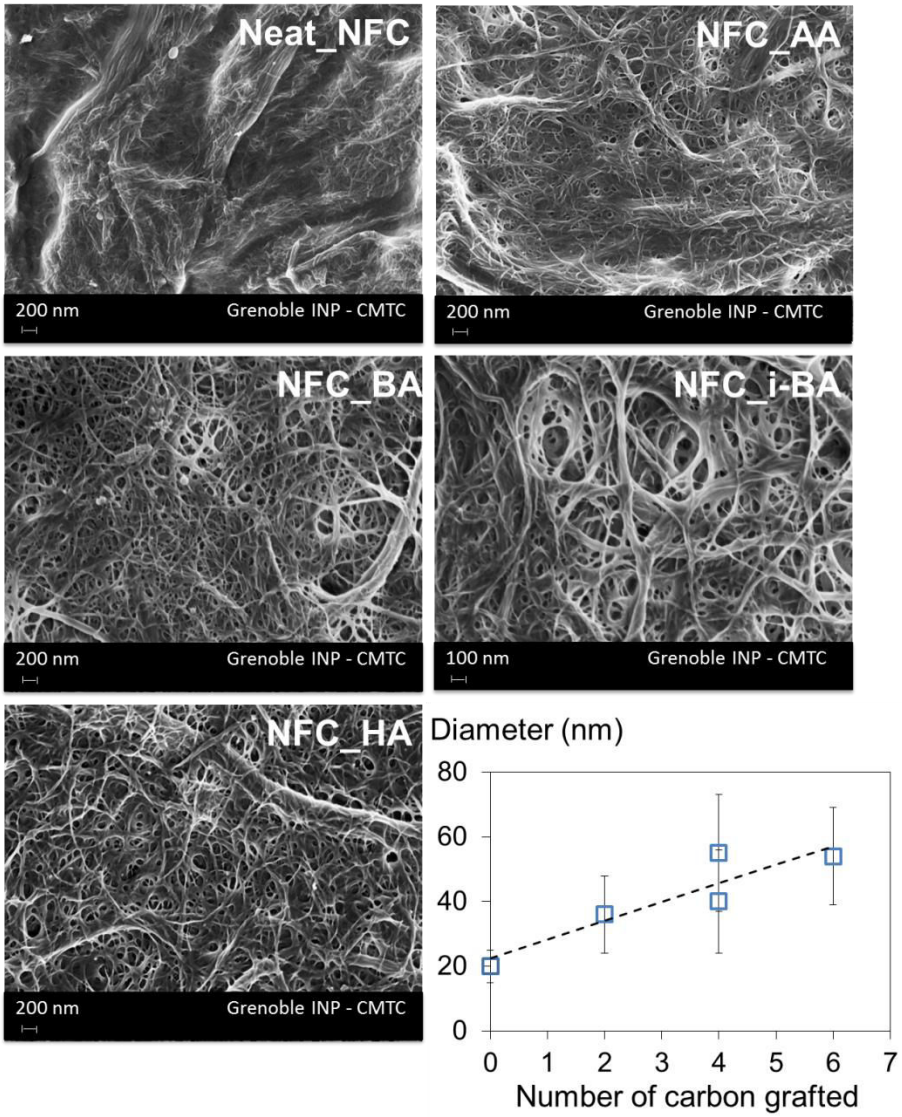


Figure 2-1 : FE-SEM pictures of neat and grafted NFC with AA (Acetic Anhydride), BA (Butyric Anhydride), i-BA (iso-Butyric anhydride) and HA (Hexanoic Anhydride)

Moreover, regarding the XPS data (presenter later) neither Fluorine nor Phosphorus peaks were detected. It was, therefore, concluded that the increase of the diameter cannot be linked to a lack of purification. Moreover, the characterization by FE-SEM is performed on dried powder of modified NFC. Then, no swelling effect can be responsible of such an increase. The slight difference in the diameter might be due to the limitation of hydrogen bonds at the outer layer of NFC. With lower intermolecular hydrogen bonds, the distance between macromolecules can increase and explain the slight increase of diameter, as proposed in Scheme 2-2 (presented in section 2.3.3).

The crystalline structure of grafted NFC and neat NFC has also been investigated by XRD, as shown in Figure 2-2. The crystallinity index is determined from equation 1 and reported in the Figure 2-2.

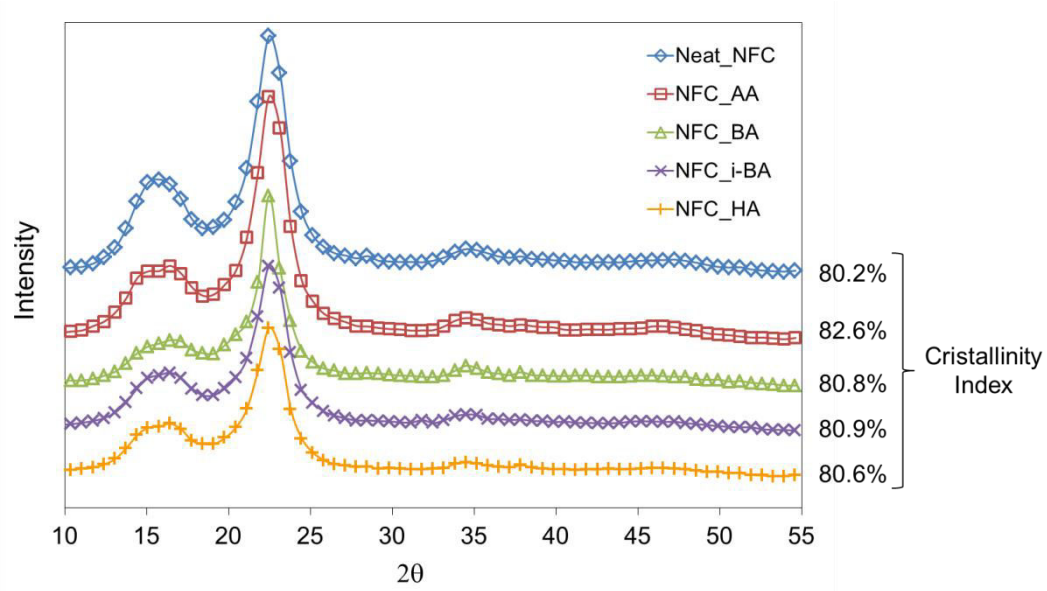


Figure 2-2 : X-Ray Diffraction spectra of neat and modified NFC and the calculated crystallinity index

The reference sample presents a similar crystallinity (80.2%) to that of the grafted ones (82.6%, 80.8%, 80.9%, and 80.6% for acetic, butyric iso-butyric hexanoic moieties respectively). This confirms the non-swelling of NFC with the ionic liquid during the surface modification. Moreover, the "peeling effect" reported by Berlioz et al. (Berlioz et al. 2009) and Cetin et al. (Çetin et al. 2009) on cellulose nanocrystals acetylation, is negligible in the case of our nanofibrillated cellulose. This is most probably due to the length of the material (higher DP), which still contains appreciable amounts of hemicellulose and amorphous cellulose, when compared with the material studied by these authors, i.e., cellulose nanocrystals.

2.3.2 Efficiency of process

To ascertain the chemical grafting, several characterizations were performed. FTIR spectroscopy was one of them. Figure 2-3 shows FTIR spectra obtained from: (a) neat NFC and NFC grafted using (b) acetic anhydride, (c) butyric anhydride, (d) isobutyric anhydride and (e) hexanoic anhydride. Before the chemical treatment, NFC display several characteristic bands attributed to cellulose macromolecules like 3496cm^{-1} (O–H), 1110cm^{-1} (C–O of secondary alcohol) (used for the normalization of all spectra) and 2868 and 2970cm^{-1} (C–H from –CH_2–).

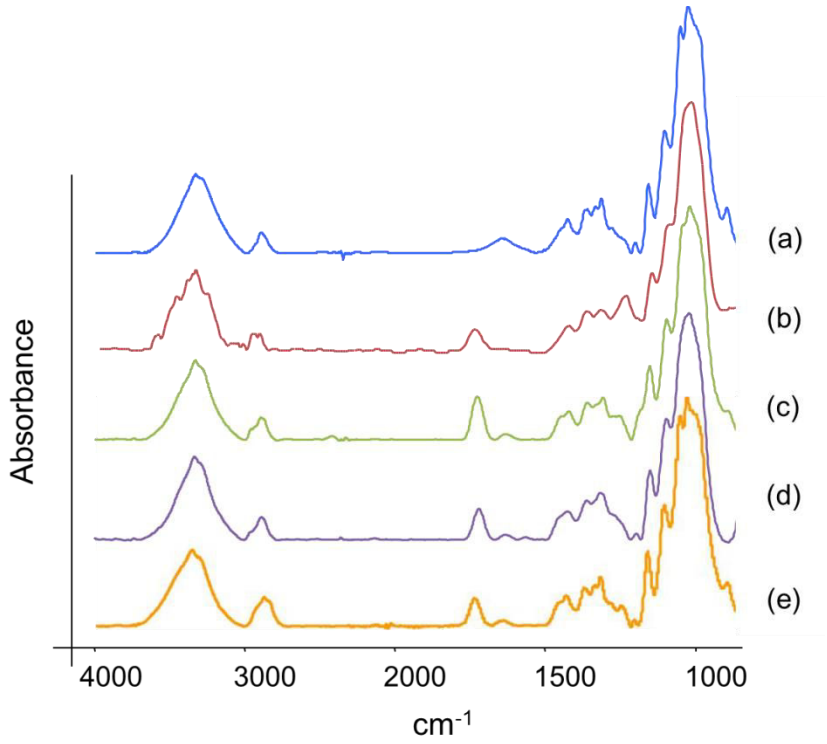


Figure 2-3 : FTIR spectra for (a) Neat NFC, (b) NFC_AA, (c) NFC_BA, (d) NFC_i-BA and (e) NFC_HA

After the esterification reaction, a characteristic peak assigned to ester bonds at 1750cm^{-1} has clearly appeared. A slight increase of the bands at 2868 and 2970cm^{-1} corresponding to asymmetric and symmetric –CH_2– stretches from aliphatic chain was also observed. We can observe the characteristic peak of water in Neat NFC before solvent exchange. This peak associated with the vibration of adsorbed water at 1650cm^{-1} slightly decreased after modification, probably because of the hydrophobic behavior of the modified material. But it is well known that cellulosic substrates are hygroscopic and the low grafting density can explain the presence of the water peak on FTIR spectra. The intensity of this peak (1650 cm^{-1}) is very low, whereas that of the signal at 3360 cm^{-1} is associated to OH function of cellulose. So FTIR measurements show some changes in the chemistry of grafted NFC after a Soxhlet extraction proving the cellulose modification.

In addition, contact angle measurements were performed in order to point out the hydrophobic behavior of the grafted nanofibers comparing to neat NFC. The results are presented in the Figure 2-4. As expected the contact angle values of a drop of water deposited on the surface of the grafted NFC are higher than those found for the neat NFC. Theoretically, the higher is the number of carbons on the grafts, higher is the contact angle value is obtained, when a low number of –CH_2 moieties is concerned. The obtained results are consistent with those expected. The neat NFC displayed a decrease of the contact angle value with the time and vanished at 20°. The values of the grafted samples are stable during

the acquisition and they are higher than those found for neat NFC surface, namely: 56°, 98.6°, 99.5° and 104.8° for acetic, butyric, isobutyric and hexanoic anhydride respectively. This trend is easy to rationalize, since long chains increase the distance between water droplet and the un-grafted cellulose polar molecules. Moreover, the fact that the contact angle tends to a value of around 100° (high grafting density and long chain), seem to support such hypotheses. The reached contact angle is close to that of polyethylene surface.

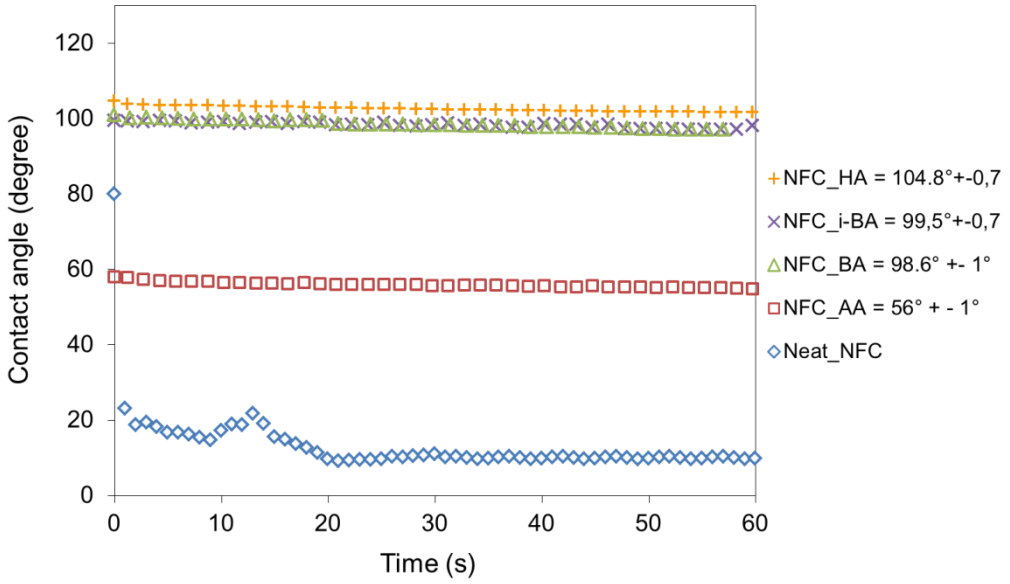


Figure 2-4 : Contact angle data for neat and modified materials

The grafted materials become much more hydrophobic than the reference unmodified counterpart, indicating indirectly that the surface grafting has indeed occurred. Elemental Analyses (E.A) was performed in order to quantify the grafting efficiency and to establish the degree of substitution (DS). The DS corresponds to the number of grafted hydroxyl function per anhydroglucose unit.

Theoretical, experimental data and DS values obtained from the elemental weight composition for neat and grafted NFC samples are reported in the Table 2-1. Theoretically, from anhydroglucose unit the weight ratio between oxygen and carbon atoms is 1.11, which corresponds to 49.4% and 44.4% for the elemental weight fraction of oxygen and carbon, respectively. However, the experimental value of weight ratio (O/C) for neat NFC is 1.26 which gives 50.59 % of O and 40.38 % of C atoms. The difference could be explained by the presence of some O-rich impurities and by experimental errors (Labet et al. 2007). The presence of hemicelluloses (generally slightly richer in O atoms) in NFC suspension can also explain this difference. A correlation proposed by previous authors (Siqueira et al. 2010b) is

used to calculate DS as previously described in the Equation 2. The results obtained are very similar with a DS of 0.3 for acetic, butyric, hexanoic anhydrides.

Table 2-1 : Calculation of the degree of substitution based on elemental analysis data

Samples	Experimental values			Corrected Values	
	%C	%H	%O	%C	**DS**
NFC acetic anhydride	42.08	6.23	47.33	45.36	**0.3**
NFC butyric anhydride	44.45	6.47	47.33	47.68	**0.3**
NFC (iso)-butyric anhydride	43.02	6.22	49.31	46.15	**0.2**
NFC hexanoic anhydride	45.59	6.69	46.04	48.90	**0.3**

The NFC modified with the iso-butyric anhydride present a slightly lower value (0.2) which could be explained by the conformation of the chemical structure of the moieties under question. In fact, only the iso-butyric graft is branched (umbrella-type) and could induce some steric hindrances.

All these characterizations tend to confirm the surface grafting of the materials. However FTIR technique has a depth of analyses superior of 1µm, contact angle is an indirect measurements and the E.A is a bulk analysis. In order to directly check the surface grafting, X-ray Photoelectron Spectroscopy (XPS) and Time of Flight Secondary Ion Mass Spectroscopy (TOF-SIMS) analyses were performed.

2.3.3 Direct measurements of surface grafting

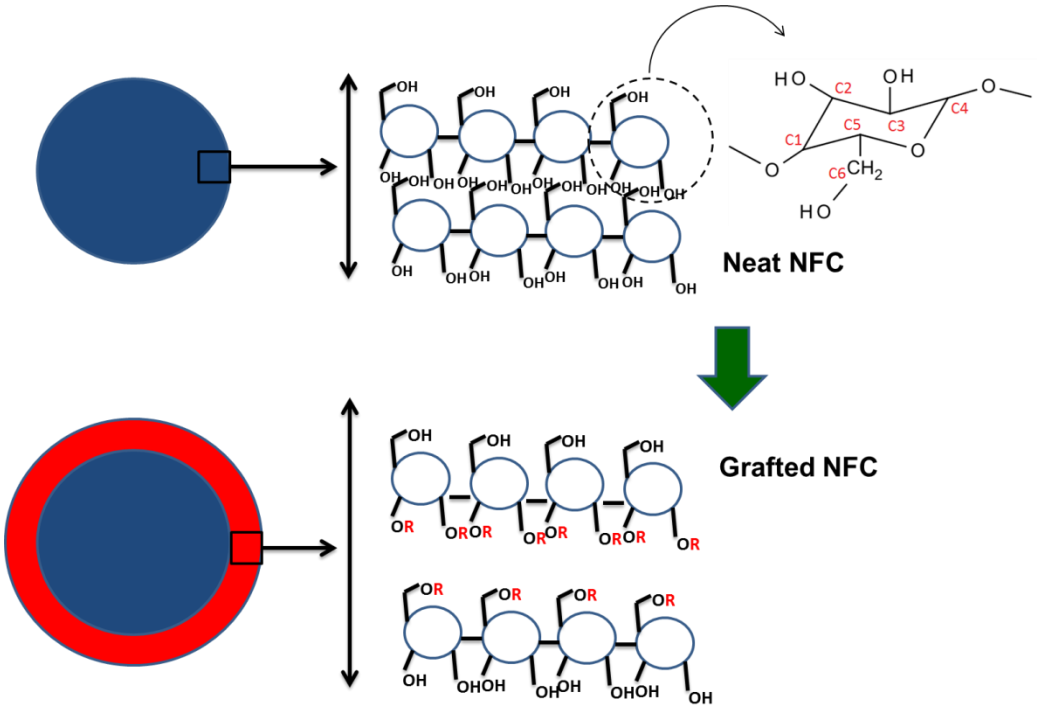
The use of X-ray Photoelectron spectroscopy (XPS) to ascertain the efficiency of cellulose surface grafting was practiced extensively the last decade, as reviewed by Belgacem's groups (Belgacem and Gandini 2009; Belgacem and Gandini 2005; Gandini and Belgacem 2011) and showed to be a very powerful technique to detect various changes at the surface.

The first relevant works dealing with the use of XPS to characterize cellulose substrates were reported by Gray's group (Dorris and Gray 1978a; Dorris and Gray 1978b; Gray 1978; Katz and Gray 1980). The deconvolution of C1s peak was reported by Ahmed et al.(Ahmed et al. 1987) showing that the different covalent bond can be associated with different carbon signal peaks.

These considerations were recently used for nanocellulose chemical grafting studied (Siqueira et al. 2010b). In theory, pure cellulose exhibits two peaks in its deconvoluted C_{1S} XPS spectra, namely:

(i) C-O at 286.7eV and associated to alcohols and ethers groups. This peak is noted as C2 and corresponds to 5 carbon atoms (C_1, C_2, C_3, C_5, C_6 in Scheme 2-2), and

(ii) O-C-O at 288.3eV attributed to acetal moieties. This signal corresponds to one carbon atom (C_4 in Scheme 2-2).



Scheme 2-2 : Anhydroglucose unit and modeling for the increase of diameter after grafting

Figure 2-5 and Figure 2-6 show, respectively, the XPS wide and the high resolution (deconvolution of C1S signal) spectra for NFC samples, before and after grafting. The wide spectra of the samples show that in all cases the main peaks are detected at 285 and 532eV, which correspond to C and O atoms, respectively. Moreover, the peak associated to O atoms is composed of 1 perfectly symmetrical peak. Therefore, it cannot be deconvoluted. It is due to an artifact during the treatments of data (in supporting information, an expansion of O atom signal for each sample is presented). No traces of ionic liquid are observed.

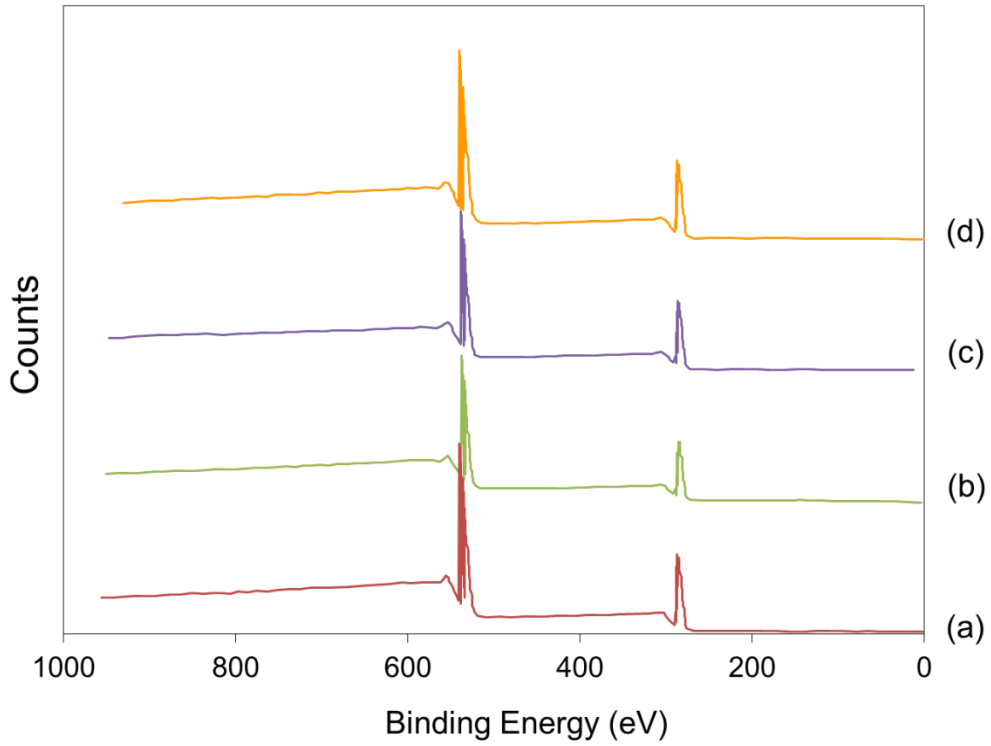


Figure 2-5 : X-ray photoelectron spectroscopy wide spectra of grafted for (a) NFC_AA, (b) NFC_BA, (c) NFC_i-BA and (d) NFC_HA

In Figure 2-6, two unexpected additional peaks are observed for cellulose reference, namely: C1 and C4. As already reported in the literature, C1 signal (285.0eV) corresponds to non-oxidized alkane-type carbon atoms (-C-C- / -C-H-) associated with the presence of residual lignin, extractive substances and fatty acids, whereas C4 peak (289.2eV) was assigned to carboxylic functions (O-C=O) originating from glucuronic acids born by hemicelluloses.

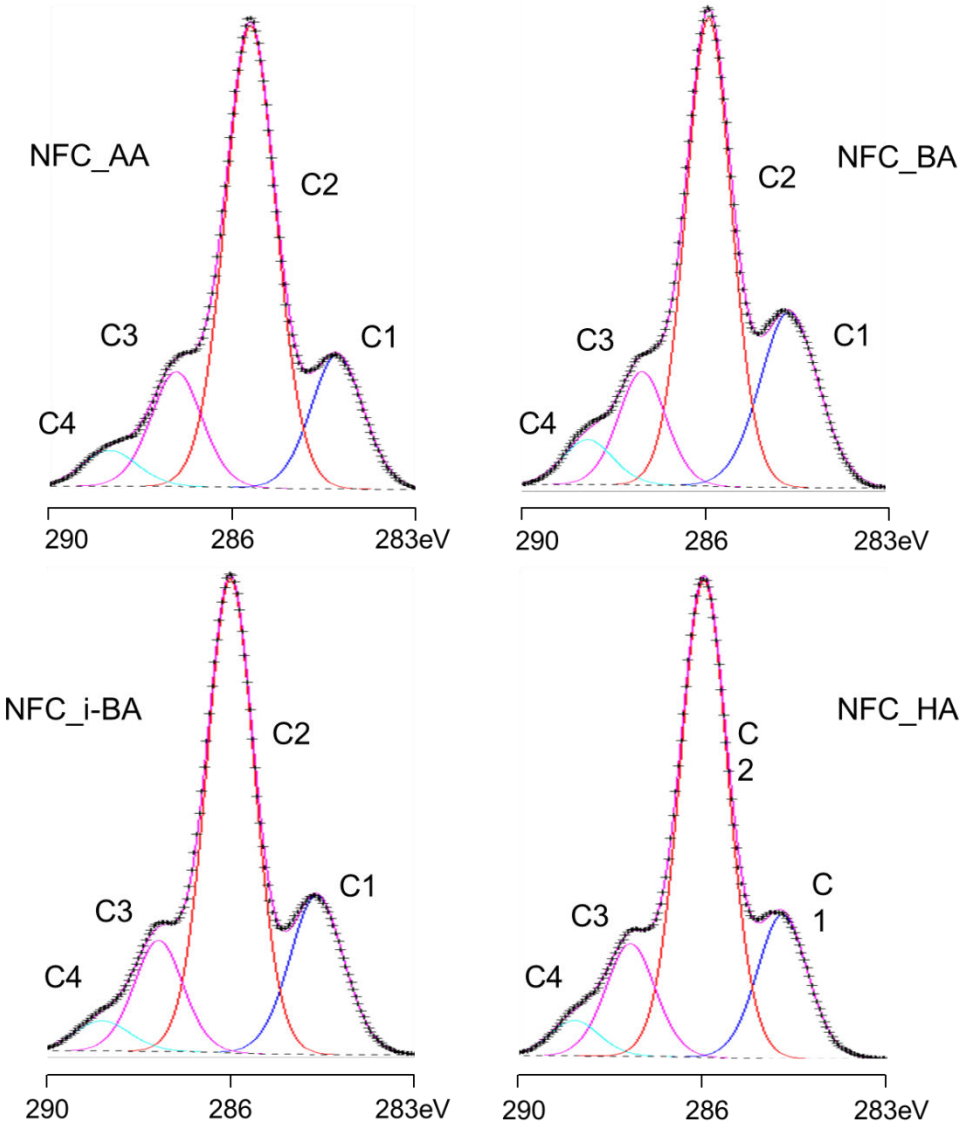


Figure 2-6 : Decomposition of the C1s signal into its constituent contribution for grafted NFCs

In these works, it was also established that the surface O/C ratio for pure cellulose (theoretical formula) is 0.83. For the majority of virgin cellulose (avicel, wood pulps, annual plants, etc.), this ratio is systematically lower, because of the presence C-rich molecular segments at the surface of the solids under study. Table 2-2 confirms this assumption, since a lower ratio O/C is found for neat NFC, i.e., 0.65. This difference could be attributed to the surface pollution by hydrocarbons adsorbed at the surface of nanofibers. Very recently, some authors assessed another explanation consisting of a sort of reorganization at the surface of NFC linked to the solvent interactions (Johannsson et al. 2011).

The ratio (O/C), reported in the Table 2-2, for all tested materials, varied when samples are grafted in comparison to neat NFC. The deconvolution of the signal C_{1S} presented in

Figure 2-6 reveals four peaks, which are attributed to C1 (C-C/C-H), C2 (C-O), C3 (O-C-O and/or C=O) and C4 (O-C=O), as already explain.

Table 2-2 : Mass concentration of each element for neat and grafted samples correlated to deconvolution of C1s

Samples	Experimental values			Deconvolution of C_{1s}						
	%C	%O	O/C	C1(%)	C2(%)	C3(%)	C4(%)	C1/C3	C4/C3	**DSS**
Neat NFC	60.6	39.4	0.65	15.1	67.8	16.8	0.4	0.90	0.02	/
NFC AA	62.8	35.7	0.57	22.6	57.2	15.0	5.2	1.5	0.3	**0.85**
NFC BA	62.1	35.8	0.58	26.0	54.5	13.6	5.8	1.9	0.4	**1.12**
NFC i-BA	62.5	35.2	0.56	19.4	61.0	14.9	4.7	1.3	0.3	**0.87**
NFC HA	61.2	37.0	0.60	22.4	59.1	14.1	4.4	1.6	0.3	**0.91**

Table 2-2 shows that the intensity of C1 (C-C/C-H) increases, from around 15 to 22%, for the virgin and grafted NFCs, respectively. Each glucose moiety possess *only* one C3-carbon, the ratio C1/C3 reflects the number of aliphatic carbons per anhydroglucose unit. The C1/C3 ratio shifted from 0.9 for neat NFC to 1.5, 1.9, 1.3 and 1.6 for the NFC grafted with acetic, butyric, iso-butyric and hexanoic anhydride, respectively. This proves the presence of grafted moieties at NFC surface. Similar analysis can be applied to C4/C3 ((O-C=O)/(O-C-O)) ratios to point out the presence of covalent bonding between NFC and anhydride. Indeed this ratio strongly increases between NFC (0.02) and grafted samples (ab. 0.35). This ratio (C4/C3) is practically stable with the increasing of the carbon number of aliphatic chain proving a slight influence of steric hindrance. Thanks to XPS data, the degree of substitution of the surface (DSS) can be deduced (Andresen et al. 2006) based on the equation 3.

The DSS is linked to the number of grafted hydroxyl function per anhydroglucose unit present at the extreme surface layer (measurements carried out on about 7 nanometers). The DSS value confirms previous assumption on steric hindrance even if butyric anhydride seems to be more reactive than the other coupling agents. This result could be associated to the lower steric hindrance and higher thermal activation and diffusion rate of this moiety. These results clearly evidence the occurrence of covalent bonding between the coupling molecules and nanofibrillated cellulose surface layer. The DSS is more or less close to 1 for each grafted samples. Thus, considering the following equation:

$$DS = \%hydroxy\,\mathrm{lg}\,roup\,at\,the\,surface \times DSS \quad \text{Eq. 4}$$

It can be established that there is approximately 20-30% of the hydroxyl groups at the surface. This is the first time that such assumption is based on experimental data and not on theoretic. An innovative and powerful technique, ToF-SIMS (Belu et al. 2003) was performed for the first time to characterize the extreme surface of NFC. This method of characterization is very surface sensitive due to the shallow depth of penetration of the ion beams. The depth is limited to the first atomic layers (max. 10 Å). Using ToF-SIMS, the molecular fragments of the different grafts could be identified

The ionization of the surface emits molecular fragments sorted according to their ratio (m/z). The source used for the fragmentation can generate positive or negative fragments. A lot of fragments can be emits. In this paper, only M^+ and M^- identified are the molecular peaks corresponding to the ionized grafted molecules (O-C-O-$R^{+/-}$). In literature (Belu et al. 2000; Mitchell et al. 2005), some specific fragments of cellulose have recently been identified. These fragments are present in the SIMS spectra and listed in Table 2-3.

Table 2-3 : SIMS characteristics cellulose fragments for neat NFC and characteristics fragments corresponding to M^+/M^- for grafted samples

Samples	m/z(-) characteristic peak of cellulose	m/z(+) characteristic peak of cellulose
Neat NFC (Cellulose fragments)	44.99 (C2H5O-)	57.07 (C4H9+)
	59.02(C2H3O2-)	115.05 (C8H3O+)
	71.02 (C3H3O2-)	127.05 (C6H7O3+)
	87.01 (C3H3O3-)	135.07 (C6H15O3+)
	101.03 (C4H5O3-)	162.08 (C6H10O5+)
	113.03 (C5H5O3-)	325.01 (C12O10H21+)
	127.01 (C6H7O3-)	530.49 (C20H34O16+)
	162.07 (C6H10O5-)	
	221.09 (C8H13O7-)	
Samples	M- fragments mass value	M+ fragments mass value
NFC AA	59.01 (C2H3O2-)	43.02 (C2H3O+)
NFC BA / NFC i-BA	87.04 (C4H7O2-)	71.05 (C4H7O+)
NFC HA	115.08 (C6H11O2-)	99.08 (C6H11O+)

At low m/z, for both positive and negative ion modes, the detected ions are very similar for all the samples. They are always cellulose characteristic peaks such as secondary ions detected at m/z(+)=57 ($C_4H_9^+$), 115 ($C_8H_3O^+$), 127 ($C_6H_7O_3^+$), 135 ($C_6H_{15}O_3^+$) and 162 ($C_6H_{11}O_5^+$) as well as at m/z(-)=45 (C_2HO^-), 59 ($C_2HO_2^-$), 71 ($C_3HO_2^-$), 87 ($C_3HO_3^-$), 101 ($C_4HO_3^-$), 113 ($C_5HO_3^-$) and 162 ($C_6H_{11}O_6^-$). The ionization of cellulose induces reorganization of the emitted fragment such as cyclization. That is the reasons why some peaks are not attributed due to the complexity of the cellulosic material.

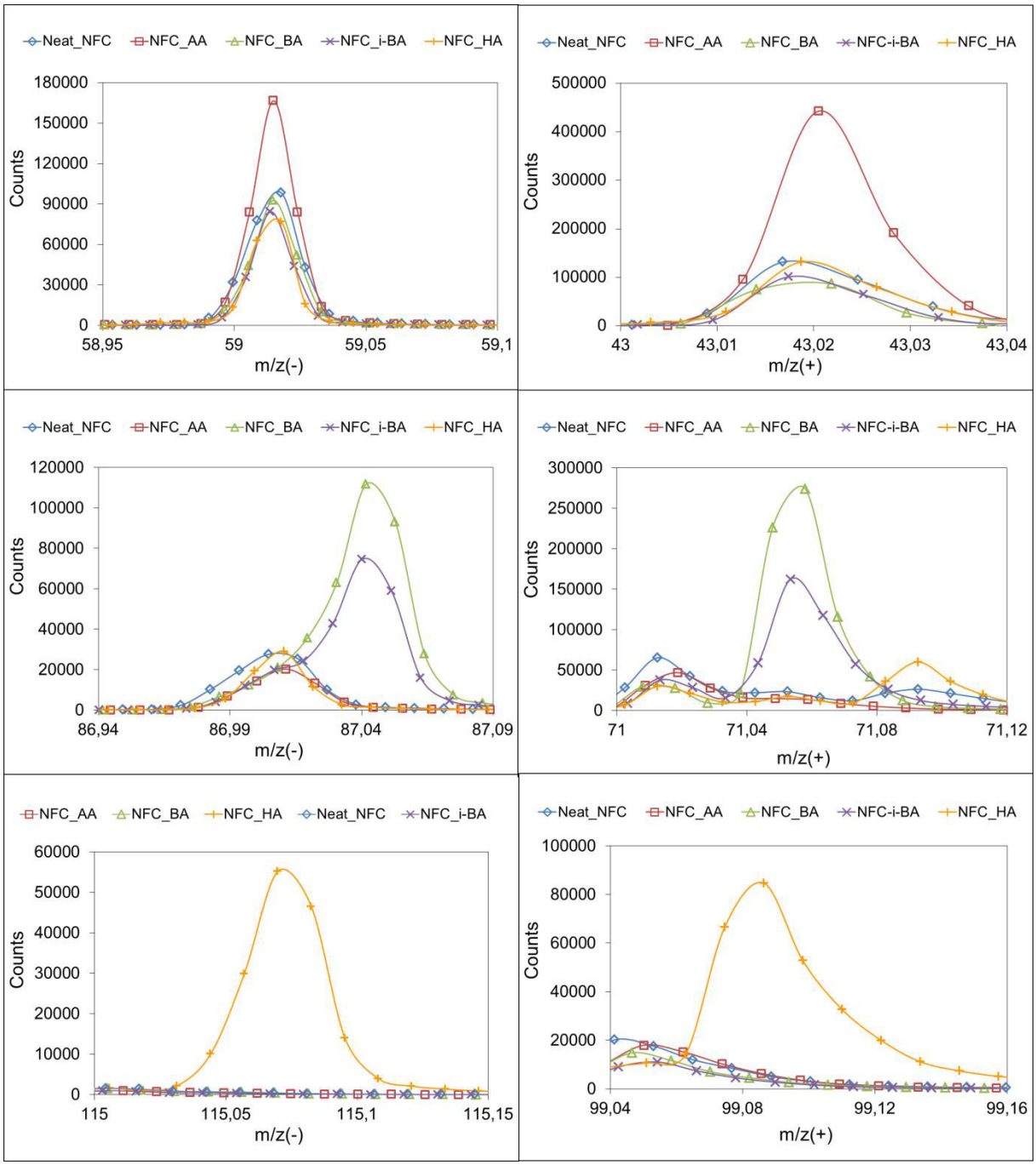


Figure 2-7 : SIMS spectra characteristic fragments corresponding to M^- (left) and M^+ (right) for grafted samples

The fragmentation is different depending on the anhydride used for the modification (Baiardo et al. 2002; Freire et al. 2006). The M+ and M- (defined before) was easily identified for all grafted samples as presented in the Figure 2-7. However additional fragments can be detected depending on grafted moiety, the ester bonds are more breakable than the others due to the depletion of electrons. Thus, M+ fragments, at m/z(+)=43 ($C_2H_3O^+$), 71 ($C_4H_7O^+$) and 99 ($C_6H_{11}O^+$) corresponding to acetic, butyric (or isobutyric) and hexanoic fragments are detected in the respective modified samples spectra (Figure 2-7). M- fragments at m/z(-)=59 ($C_2H_3O_2^-$), 87 ($C_4H_7O_2^-$) and 115 ($C_6H_{11}O_2^-$) corresponding to acetate, butyrate – isobutyrate and hexanoate moieties, are also mostly detected, except for the first one which doubles in intensity.

Indeed the sample grafted with the acetic anhydride is the most difficult case to discuss. All signal corresponding to this samples coincide with the cellulose fragments or the other grafted materials. But in this case the characteristics peaks' (M^+ / M^-) intensities of this sample are two times higher than other signals. These observations confirm the grafting of this sample. These results clearly show the occurrence of extreme surface grafting coupling molecules and nanofibrils cellulose. This is the first time that TOF-SIMS method is used for the characterization of NFC surface modification.

2.3.4 Recyclability of IL

The challenge of this new method for chemical surface modification consists of limiting the use of hazardous organic solvents. The reaction was performed in bmimPF_6 as reaction media avoiding volatile organic compounds but also favoring solvent recycling. After the chemical reaction, the IL was recycled as shown in Scheme 2-1. Liquid extraction was carried out after each reaction and the purification was first followed by FTIR. Only the different purification steps of IL used for the chemical surface modification performed with acetic anhydride is presented in the Figure 2-8.

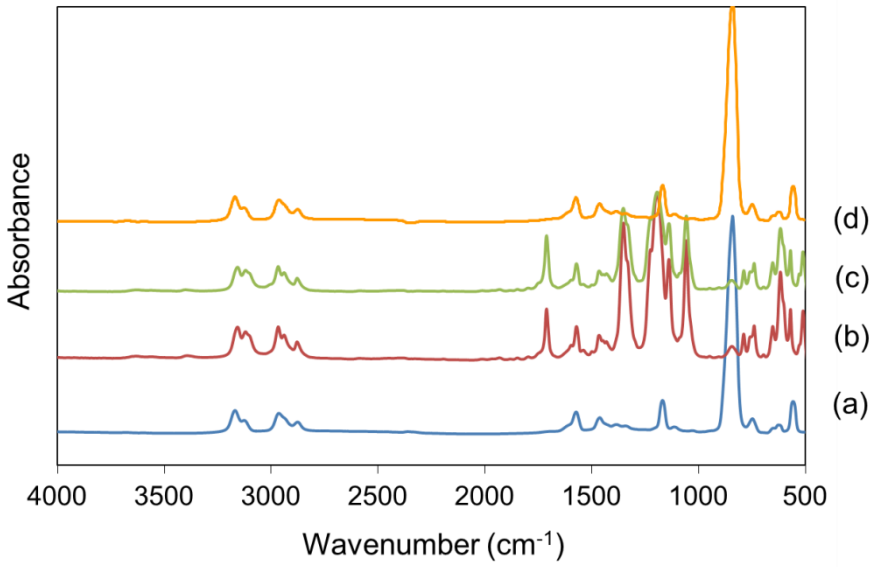


Figure 2-8 : IR spectra of the different steps used for purification of the IL after acetic anhydride reaction: (a) IL pure, (b) NaOH x1, (c) NaOH x2 and (d) ethylic ether

After the two extractions with sodium hydroxide solution there is some residual acid generated during the reaction (ν_{-COOH} = 1700cm^{-1}). After extraction with diethyl ether, no peakcorresponding to the vibration of acid groups are detected. Figure 2-9 represents the FTIR spectra of all purified IL used for each chemical modification. Thus, no residual acid groups are presents in the IL. The yield of recovery is 92% in comparison to the initial IL used for the reaction.

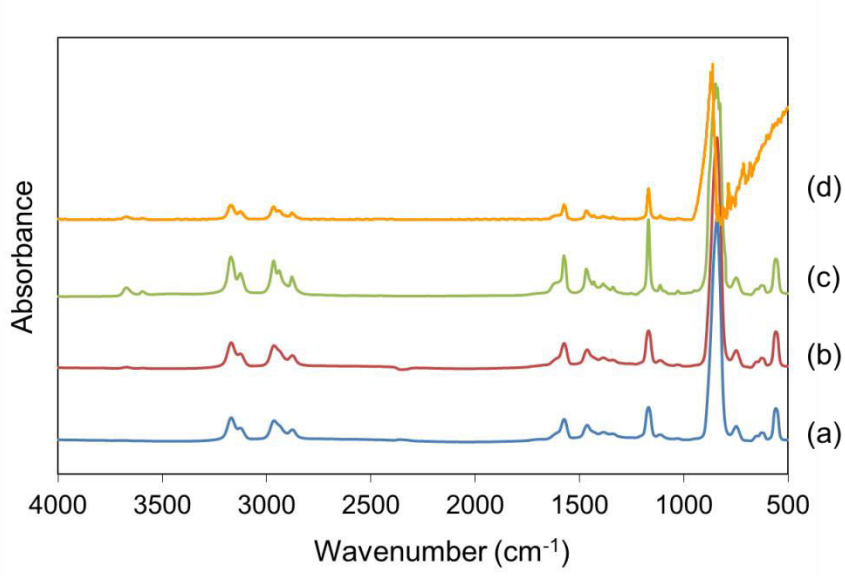


Figure 2-9 : FTIR spectra for (a) IL pure and for IL recycled after (b) acetic, (c) butyric and (d) hexanoic anhydride grafting

Quantitative ^{1}H, ^{13}C, ^{19}F and ^{35}P NMR analyses were performed to confirm more accurately the purity of the recycled IL. Figure 2-10 shows, that chemical shifts, integrals and

hyperfine structure between pure and recycled IL are recovered unchanged. From ^{1}H and ^{13}C spectra, the cationic chemical structure could be deduced unmodified, while ^{19}F and ^{31}P spectra show the conservation of the PF_6^- anionic nature with the characteristic doublet ($^{1}J_{FP}$ = 711Hz) at -70.02 ppm and the heptuplet ($^{1}J_{FP}$ = 711Hz) at -138.3 ppm for fluorine and phosphorus respectively. Moreover, some differences on peaks at 0.8, 1.3 and 1.8 ppm can be observed. This is only due to the scanning of the figure which decreases the resolution. However, in supporting information data, readers can find the expansion of this range of ppm from 0 to 2 ppm, which points out the exact correspondence between pure and recycle IL.

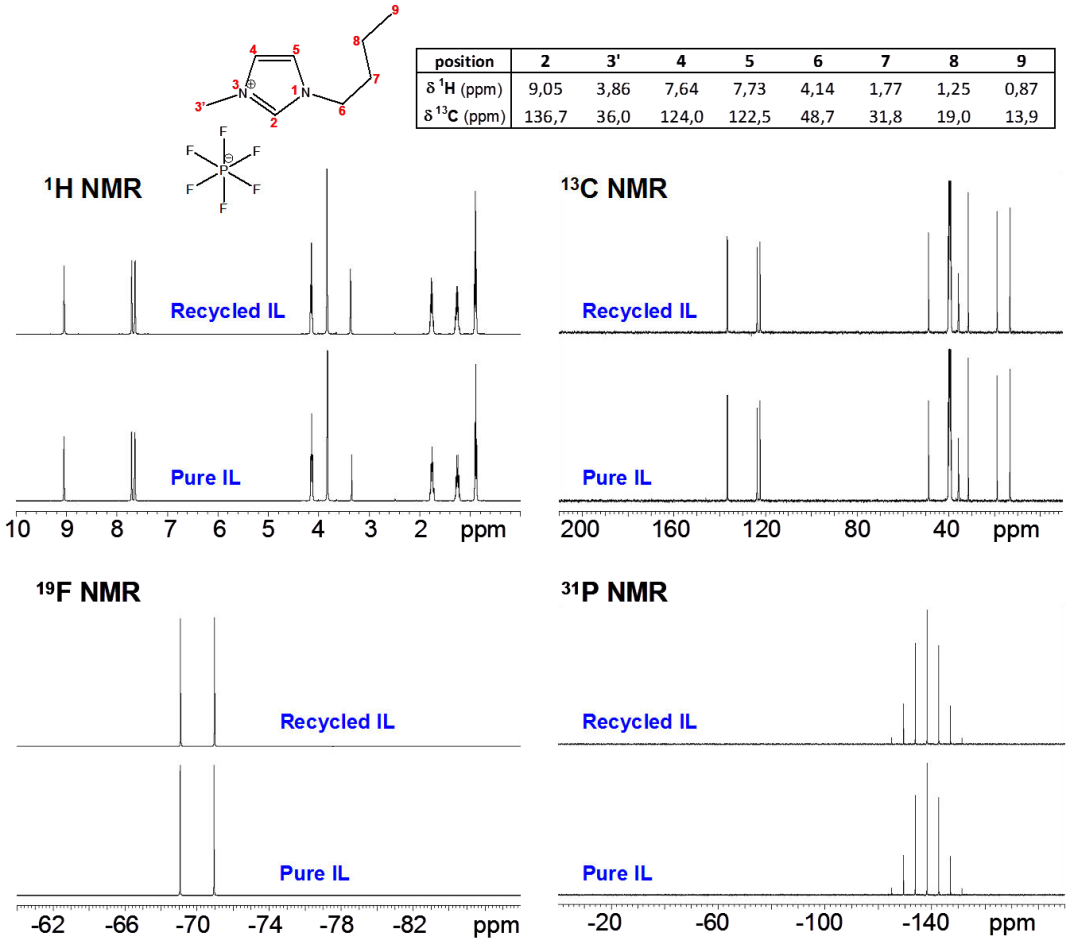


Figure 2-10 : NMR spectra of pure and recycled IL for each nucleus (^{1}H, ^{13}C, ^{19}F and ^{31}P)

The peak at 3.8 ppm is associated to the water absorbed by the DMSO-d6 which is extremely hygroscopic. The degree of purity can be assessed from ^{1}H spectrum of recycled IL: sensitivity was increased till ^{13}C satellites (0.5% intensity of the corresponding signal) and no impurities are observed on Figure 2-11.

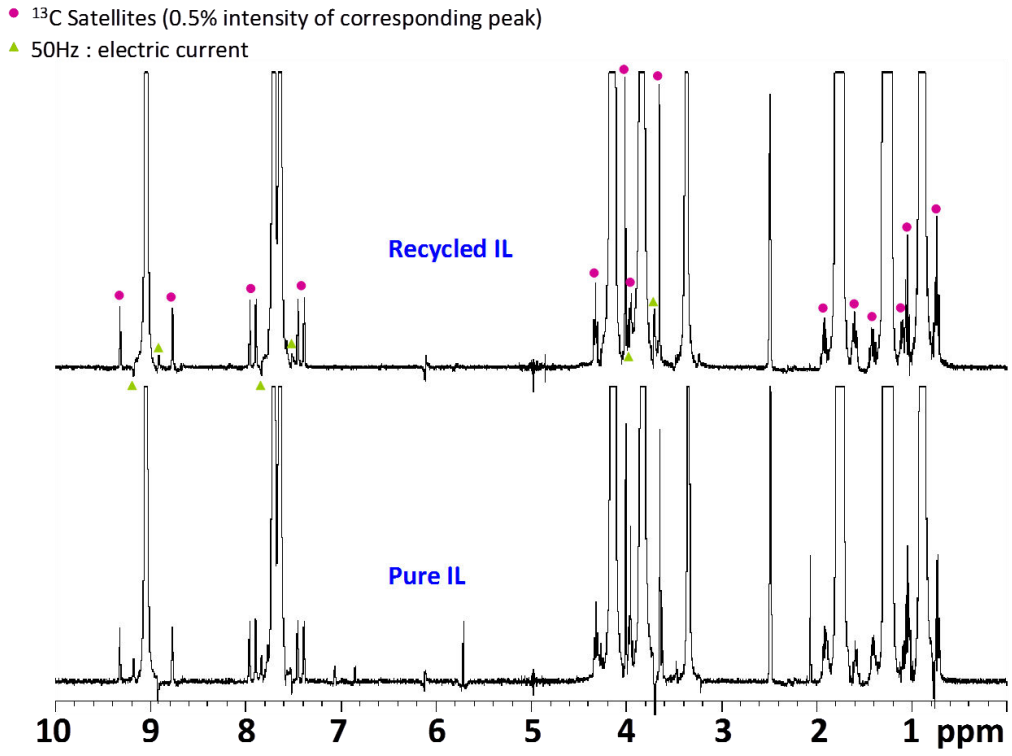


Figure 2-11 : ^{1}H NMR spectra of recycled and pure IL – full circles indicating the ^{13}C satellites

The initial structure is conserved and no changes are observed. Thanks to liquid extraction developed, the IL is completely recycled without any impurities or by-products formed during the reaction. Thus, in order to limit the uses of volatile solvents and decrease chemical reaction cost (by recycling), the ILs can be envisaged as media for this surface chemical grafting. However For the recycling process organic solvent (ethyl ether) have to be used to recycle this ionic liquid, which limits the “green” impact of the process. Other solutions like by-products evaporation or condensation have been tested but without appreciable success to reach pure IL. Work with reagent producing fewer by-products (e.g. isocyanates) could be another solution.

2.4 Conclusion

This paper shows clearly that using a “green” solvant (Ionic Liquid) could give rize to an efficient grafting of nanoscaled cellulosic substrates without affecting their morphological properties. Moreover, it shows that, at the end of the reaction, the IL could be recovered and recycled pratically quantitatively. The use of several techniques to assess the quality of the recycled IL was performed and showed that the resulting recycled solvant is quite pure and ready to be used for a next cycle of chemical grafting. Moreover, chemical grafting were efficient and induced substantial changes in the surface properties of NFC. To the best of our knowledge, the ToF-SIMS was applied for the first time to demonstrates the occurrence of the grafting between cellulosic nanofibrils and various anhydrides. Thus, these analyses gave clear-cut evidences about the grafted molecules and confirmed the results deduced from other common techniques, such as FTIR, EA, or more specific one like XPS. This is the first study using Ionic Liquid for efficient heterogeneous grafting of NFC surface. These promising results could help the scaling-up chemical modification of NFC, creating different grade for NFC.

Acknowledgments

This research was supported by the “Scale-Up of Nanoparticles in modern PAPermaking” (SUNPAP) project of the seven framework program of European research. The ToF-SIMS measurements were funded by the French ANR “RTB Exogène” project.

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3. Water Based reaction CONFIDENTIAL – Patent in progress

Due to start-up creation, we have chosen to keep confidential this part. A patent in still in progress and of course cannot be present in this manuscript.

Suite à la création d'une start-up, la partie initialement traitée ici est soumis à confidentialité due au dépôt d'un brevet.

Nous avons donc choisi de retirer cette partie du manuscrit.

Figure captions

Table captions

Scheme captions

Chapter III.

End-Uses of modified NFC

Résumé Français – French Abstract

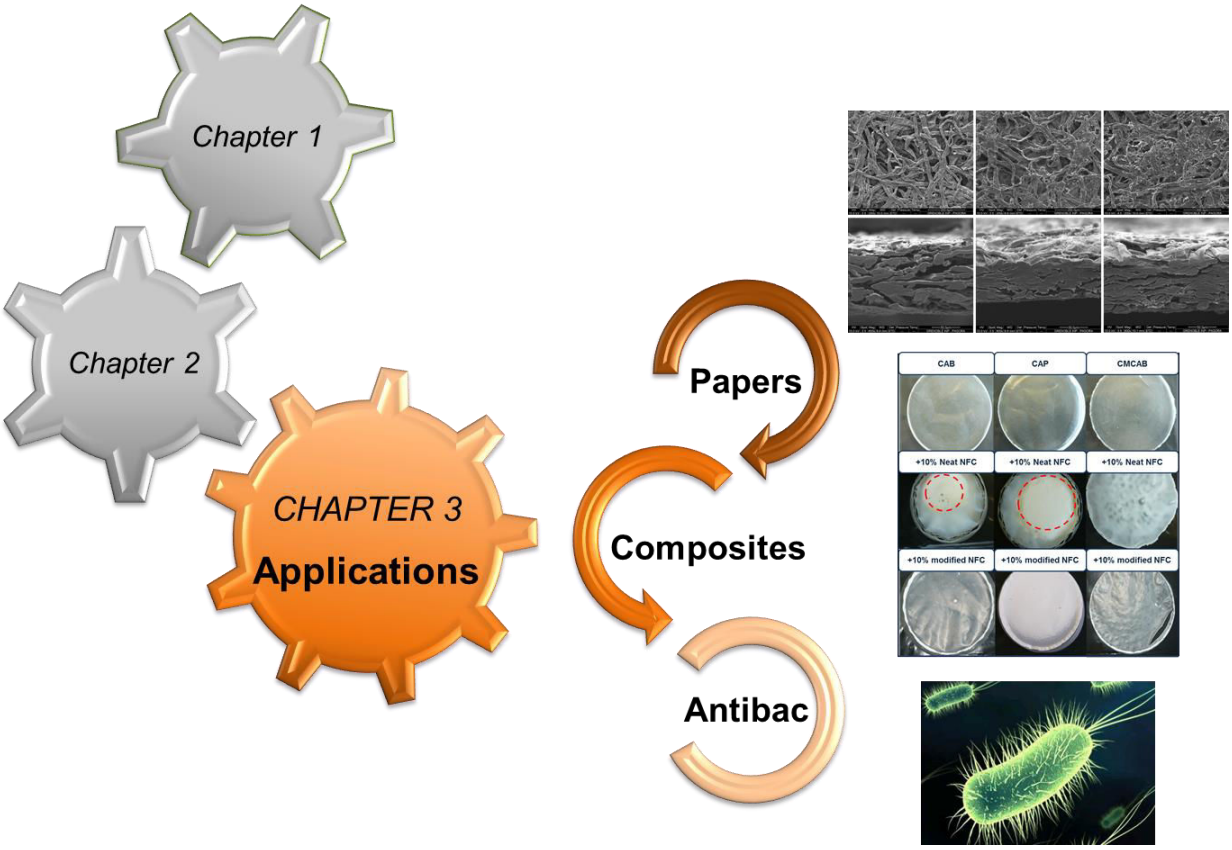

Figure 1-1 : Représentation schématique de l'organisation de la partie 3 du projet de thèse

Comme nous venons de le voir dans le Chapitre 2, les nanofibrilles de cellulose ont été modifiées selon 3 types de greffage, sans observer de différences importantes de morphologie et structure mais avec des propriétés de chimie de surface complètement différentes.

Dans ce Chapitre 3, nous avons donc voulu utiliser et valoriser ces nouveaux types de NFC dans 3 champs d'applications distinctes : dans le domaine du papier, celui des composites et enfin celui des matériaux antimicrobiens.

Dans la première partie de ce chapitre (**Papier 4** - *Accepté dans Industrial Crops and Products - 2013*), les NFCs greffées via de l'AKD ont été introduites en masse dans du papier à différents ratio massique. L'objectif de cette étude est à la fois d'augmenter les propriétés mécaniques du matériau mais également de conférer au papier un caractère hydrophobe.

L'un des points importants de cette étude réside dans la quantification de la rétention réelle des NFC (modifiées ou non) dans le matelas fibreux. Les caractérisations du complexe

« fibres de cellulose/NFC », ont montré l'intérêt d'utiliser des nanofibrilles de cellulose afin de renforcer les propriétés mécaniques du papier. De plus, les NFC modifiées apportent, elles, clairement un plus avec le renfort mécanique mais aussi un comportement hydrophobe. Ainsi, il a été prouvé pour la première fois que l'emploi de NFC modifiées chimiquement permet au matériau ainsi produit d'être plus résistant mécaniquement tout en ayant des propriétés hydrophobes requises dans certaines applications.

Afin de développer des applications à hautes valeurs ajoutées, il a été décidé d'utiliser les nanofibrilles modifiées par la stratégie employant les liquides ioniques dans les composites. La deuxième partie de ce chapitre (**Papier 5** - Soumis dans *Composites Part A: Applied Science and Manufacturing – 2012*) est donc dédiée à l'utilisation de nanofibrilles de cellulose modifiées dans une matrice de dérivé de cellulose pour créer un monomatériau cellulose en favorisant un continuum à l'interface renfort/matrice.

Pour ce faire, 3 dérivés cellulosiques : CAB – CAP – CMCAB, ont été étudiées. L'idée première était d'utiliser les NFC modifiées disposant de greffons de faible longueur en carbone (C_2, C_4 et C_6) pour maximiser la compatibilité entre la matrice et les éléments de renfort.

En effet, un composite entièrement fait de matériaux issus de ressources renouvelables a été préparé. L'emploi de NFC dans des matrices de dérivés de cellulose a permis d'augmenter de manière significative les propriétés thermomécaniques des bionanocomposites. L''ajout de 10% massique de NFC natives ou modifiées permet d'augmenter le plateau caoutchoutique de 10 à 30°C selon le type de matrices ou éléments de renforts utilisés. Il est important de noter que la dispersion des NFC modifiées conduits à un film beaucoup plus homogène que ceux obtenus avec des NFC vierges mais avec des renforts légèrement plus faibles. Ainsi on a pu montrer dans cette étude que plus le réseau est structuré par des liaisons hydrogènes, plus les propriétés thermomécaniques sont augmentées.

Nous avons donc pu également étudier l'impact de ces NFC modifiées en tant qu'agent antibactérien et suivre dans un second temps la biodégradabilité de ces éléments (**Papier 6** Accepté dans *Materials Science and Engineering C – 2013*).

Cette étude montre pour la première fois des résultats très intéressants et prometteurs qui pourrait être utilisés dans des applications à fortes valeurs ajoutées. En effet, il est démontré que les NFC modifiées peuvent être considérées, comme des agents antibactériens (ou au moins bactériostatique) tout en conservant leurs propriétés de biodégradabilité.

Les traitements chimiques appliqués sur les NFC ont permis de développer une activité antibactérienne vis-à-vis de bactéries de type Gram+ ou Gram-. Cet effet peut varier en

fonction du greffon. Qui plus est, une certaines synergie lorsque des nanoparticules de TiO_2 sont ajoutées, a été démontrée.

La biodégradabilité des échantillons a ensuite été testée. Selon le type de greffage, on peut conserver ou contrôler la biodégradabilité du matériau final. Une telle étude ouvre un large spectre d'application et devrait être complétée par d'autres types de greffage et en étudier l'impact dans un matériau final.

Ce chapitre 3 propose donc une avancée significative dans les applications de nanofibrilles de cellulose modifiées avec des résultats prometteurs fonction des différentes stratégies utilisées pour la modification chimique. Comme précédemment exposé, les nanofibrilles de cellulose constituent donc un matériau innovant avec une large palette d'application. Certains effets peuvent être ainsi contrôlés et on peut en adapter les propriétés finales une fois dans un matériau.

English Abstract – Résumé Anglais

As we have seen in Chapter 2, the nanofibrillated cellulose were modified according to three types of grafting, without observing significant differences in morphology but with different surface chemistry properties.

In this Chapter 3, we have tried to use these chemically modified NFC in three distinct fields of application. Indeed, we have applied these modified NFC in (i) the paper to see the influence on the final properties of the material but also in (ii) cellulosic composites or (iii) antimicrobial materials.

In the first part of this chapter (**Paper 4** - Accepted in *Industrial Crops and Products - 2013*), NFCs grafted by an AKD emulsion introduced in the bulk of hand-sheet paper at different mass ratio and compared to those obtained with neat NFC. Indeed the context of this study is to increase the mechanical properties of the hand-sheet but also to give to the paper a hydrophobic behavior.

One of the critical points of this study is the quantification of the actual retention of NFC (modified or not) in the fiber mat. The characterization of the complex "cellulose fiber / NFC" showed interest in using cellulose nanofibrils to enhance the properties of paper. In addition, modified NFC have clearly shown a hydrophobic behavior. Actually it has been proven for the first time that the use of modified NFC allows the material to be more resistant while having hydrophobic properties required in some applications.

To develop applications with higher added value, it was decided to use the nanofibrils modified using ionic liquids in composites. The second part of this chapter (**Paper 5** - Submitted in Composites Part A: Applied Science and Manufacturing - 2012) is dedicated to the use of modified cellulose nanofibrils in a matrix of cellulose derivative.

Three cellulosic derivatives: CAB - CAP - CMCAB were studied. The first idea was to use NFC grafts modified with short length carbon (C_2, C_4 and C_6) to maximize compatibility between matrix and reinforcing elements.

Composite material made entirely from renewable resources was prepared. As expected; use of NFC in these matrices significantly increased the thermomechanical properties of bionanocomposite. Furthermore the addition of 10 %wt. native or modified NFC increases the rubbery plateau of 10 to 30 ° C depending on the type of matrix or reinforcing elements used. It is worth to note that better dispersion is achieved with modified NFC but slightly lower reinforcement is obtained. Thus it proves that the more the network is structured by hydrogen bond the more thermomechanical properties are increased.

Then the impact of these modified NFC as an antibacterial agent has been assessed and followed in a second step by checking the biodegradability of these elements (**Paper 6** - Accepted in *Materials Science and Engineering C* - 2013).

This study shows for the first time very interesting and promising results that could be used in applications with high added value. In fact, most of modified NFC can be considered as antibacterial agents, while maintaining their biodegradability properties. Chemical treatments applied to the NFC helped developing antibacterial activity against bacteria Gram + or Gram. A synergistic effect when TiO_2 nanoparticles are added has been also evaluated. The biodegradability of the samples shows that we can conserve or control the biodegradability of the final material. This study opens up a wide spectrum of application and should be supplemented by other types of grafting and by studying its impact in the final material.

This chapter proposes three advanced applications using modified cellulose nanofibrils with promising results. As previously stated, the cellulose nanofibrils are therefore an innovative material with a wide range of application. Some effects can be well controlled and you can adjust the final properties once in a material thanks to the chemical grafting.

Chapter III.

1. Effect of chemically modified nanofibrillated cellulose addition on the properties of paper

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Abstract

In the present work, nanofibrillated cellulose (NFC) has been chemically modified by nanoemulsion process. Surface chemical modification has been proved by FTIR. Modified NFCs have been added in wet-end paper process for the first time and ensued fibre-based materials properties have been measured. Mechanical reinforcement is observed whatever the NFC (treated or not). With 16 %wt. of modified NFC, Young's Modulus and Breaking length increase of 72% and 51% respectively. Air permeability strongly decreases with modified NFC. The main advantage is the strong diminution of water absorption (divided by more than 6). The synergy of such properties is very difficult to achieve and this new strategy opens the field of several application like barrier material or filtration.

Keywords

Nanofibrillated cellulose – chemical modification – fiber-based material – Mechanical properties- Air permeability - water absorption - paper

***Inspired from**: Karim Missoum, Florian Martoïa, Naceur Belgacem Julien Bras – Industrial Crops and Products (2013) – Accepted*

1.1 Introduction

Nowadays there is a growing interest for developing bio-based and efficient materials. To achieve this strategy, last decade has seen the emergence of new bio-based nanoelements extracted from several polysaccharides (e.g. cellulose (Lin et al. 2012), starch (Le Corre et al. 2010), and chitin). Cellulose-based nanoparticles are far away the most developed and several kind of “nanocellulose” can be distinguished depending on the chemical or the mechanical pre-treatment subjected to starting cellulose fibers. Recent reviews (Eichhorn et al. 2010; Habibi et al. 2010; Isogai et al. 2011; Moon et al. 2011; Siró and Plackett 2010a) give a good overview on this family and its main properties. This study will focus on one type of nanocellulose: the nanofibrillated cellulose (NFC) obtained by enzymatic pre-treatment followed by high shear mechanical treatment. They consist of aggregates of cellulose microfibrils and their diameter is in the range of 20-50 nm with a length of several micrometers. Contrary to cellulose nanocrystals, NFC exhibit both amorphous and crystalline parts and present a web like structure. Their key properties are their high specific area, their ability to establish hydrogen bonding and their high aspect ratio, which leads to possible entanglement. These properties yield transparent nanoporous films once dried and gel-like suspension at low concentration in water. This bio-nanomaterial was first of all used essentially in nanocomposites for their reinforcement property (Siqueira et al. 2010b; Siqueira et al. 2008). Their nano-scale dimensions and their ability to form a strong entangled nanoporous network allow emerging new high-values applications like aerogels or barrier films as very recently detailed in a review (Lavoine et al. 2012). Moreover, last years, huge amounts of studies aiming optimizing their productions have achieved real breakthrough which makes their industrialization expected in the coming years.

Innovative researches with these NFC concern their surface chemical grafting to provide them added-value properties. Only few papers dealt with this strategy and toxic solvent (or reagents) or solvent exchange processes are usually proposed (Lonnberg et al. 2011; Siqueira et al. 2010a; Stenstad et al. 2008). Only recently, new green approach has been proposed using: (i) click chemistry in water (Filpponen et al. 2012), (ii) ionic liquid (Missoum et al. 2012a), (iii) solvent-free process (Berlioz et al. 2009; Rodionova et al. 2010) or (iv) nanoemulsion concept (Missoum et al. 2012b). The application of such functionalized NFC is still under investigation in most of cases and to the best of our knowledge nobody used hydrophobically modified NFC to produce fiber based material like paper.

Paper materials are highly present in our society for edition or packaging industry. This fibrous material is even one third of materials used for packaging. It is already biodegradable and bio-based. However main mechanical and barrier properties are usually obtained with

petroleum-based chemicals added to the bulk of paper web (called wet end chemistry), by impregnation or by coating. In this study, the modified NFC will be added to the bulk before forming the web-like structure. At this place, the product classically used is also quite expensive and several parameters like absorption, retention are of high importance.

In 1983 Turbak et al. (Turbak et al. 1983) have discovered NFC and suggested their use in papers, and only about 25 years later such applications have appeared. Indeed the combination of NFC and papers is recent and only few scientific papers are nowadays published on this thematic in spite of several collaborative projects (e.g. SUNPAP in Europe, ArboraNano in Canada) and industrial projects. Mainly conference proceedings (Hamann 2011; Luu et al. 2011) and patents (Heiskanen et al. 2012; Laine et al. 2012) are available. It seems admitted that NFC could strongly improve the mechanical properties of papers if added in bulk(Eriksen and Syverud 2008; Da Silva Perez et al. 2010). However such an improvement is quite similar to refining process used in paper industry(Hamann 2011). They could also clearly improve barrier properties if used in coatings (Aulin et al. 2012; Rodionova et al. 2012; Syverud and Stenius 2009).The first studies show the interest of this combination in applications such as food packaging or printing (Bilodeau 2012; Hult et al. 2010; Spence et al. 2010). Nevertheless most of the researches are dealing with use of NFC as coating materials and to our knowledge none of them used chemically modified NFC added in the paper bulk.

The target of this study was, therefore, to assess the influence of the addition of chemically modified NFC into the fiber mat. The main idea was to provide new properties.

1.2 Experimental

1.2.1 Materials

The wood pulp was kindly delivered by Domsjö (Sweden) and corresponded to a mix between Spruce and Pinus (60% and 40%, respectively). This material is a dissolving pulp referred to sodium based sulfite mill extraction.

Pure liquid AKD (without stabilizer) was kindly supplied by Hercules (Prequel 9000), as AKD micro-emulsion (Aquapel) which corresponded to a cationic starch-stabilized commercial emulsion.

Chloroform and Tetradecyltrimethylammonium Bromide (TTAB) was purchased from Sigma Aldrich (France), as well as ethanol and acetone. All chemicals were of high purity and used as received without further purification. Deionised water was used in all experiments.

1.2.2 Nanofibrillated Cellulose

Nanofibrillated cellulose suspension was produced from Domsjö pulp. A suspension of bleached Domsjö fibers (2.0%wt.) was enzymatically pretreated with endoglucanase (Cellulase) during 1h at 50°C. Then, the slurry was fibrillated using a Masuko Grinder© (Japan). Size reduction of the fibers into nanofibrillated cellulose was obtained after 10 passes between the rotating and the static stones at 1,500 rpm. Solid content of the NFC suspension was around 2.6% (w/w).

1.2.3 Nano-emulsion preparation and adsorption onto NFC

In a one hand, a cationic surfactant (TTAB) solution was prepared by dissolving 12.11g in 1L of deionized water during 1hour. This quantity is ten folds the critical micellar concentration (CMC). In another hand, pure liquid AKD is diluted in chloroform (i.e. the “oil phase”) at a concentration of 550g.L^{-1}. Then, 14.8g of the AKD/Chloroform solution was added to 50 g of the surfactant solution (TTAB + water). The mixture is then sonificated during 2 min at 20% of the maximum power of a Branson 450 Sonifier® apparatus (United States). The obtained emulsion is then placed in a pre-heated oil bath at 70°C, in order to remove chloroform during 20 min, thus yielding the nanoemulsion.

Nanofibrillated cellulose suspension at a concentration of 2.6% (w/w) was mixed with the nanoemulsion during 30 minutes, in a pilot reactor of 15 L with controlled mechanical shearing of 500rpm. After the adsorption process, the final suspension is stored at 4°C before being used. Figure 1-1 summarizes the different steps described above.

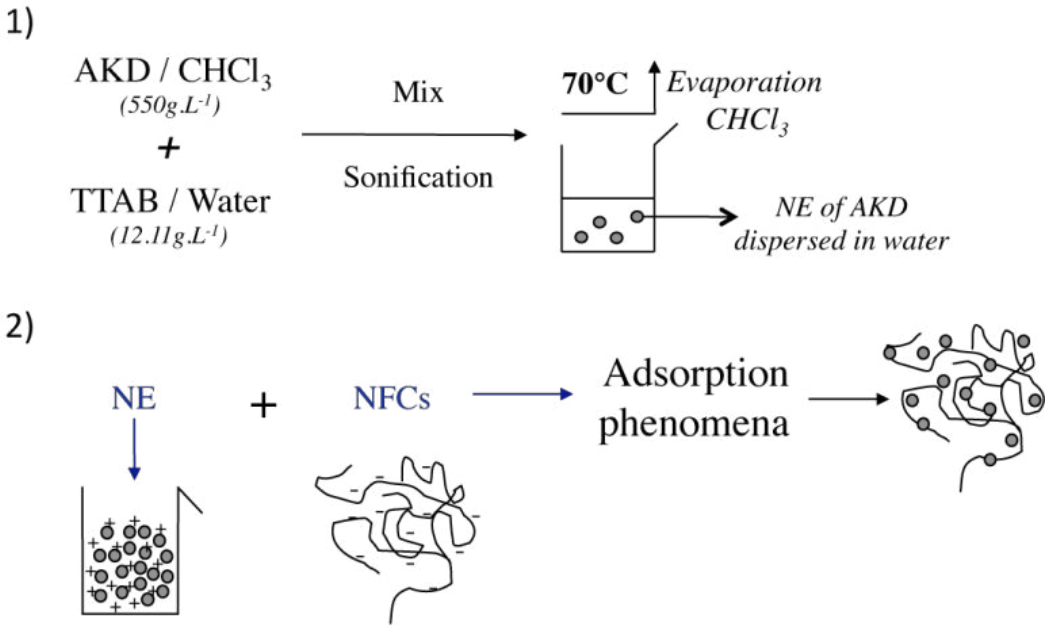

Figure 1-1 : Preparation and adsorption step of nanoemulsion onto NFCs

1.2.4 Preparation of papers reinforced with cellulosic nanofillers

Sheets were filled with 5, 10, 20, 30, and 50% of untreated or AKD-modified NFCs. The suitable amount of NFC suspension at 2%wt. was added to the pulp slurry. The pulp suspension was obtained from non-refined Domsjö pulp kept overnight in water and re-dispersed with a pulper at a concentration of 2g.L^{-1}. The suspension (fiber + NFC) was then strongly stirred with a blender during 30s, in order to obtain a homogeneous suspension. Each sample was prepared by taking out 1L of the fibrous/NFC suspension. Then, hand-sheets were performed through vacuum-filtrated system supplied by Rapid Köthen. After filtration, wet hand-sheet were first pressed in order to remove residual water and then carefully peeled off from the filtration grid and staked between two filter papers.

Finally paper sheets were obtained after vacuum-assisted drying at 80°C for 10-15 minutes. For papers treated with modified NFC an additional heating step was performed at 120°C for two hours, in order to complete the esterification reaction between AKD and cellulose, using a contact drying (glazing apparatus).

1.2.5 Characterizations of neat and modified NFC

Scanning Electron Microscope equipped with a Field Emission Gun (SEM-FEG), model Zeiss Ultra column 55 Gemini, was used to observe untreated and modified NFCs. The accelerating voltage (EHT) was 3 kV for a working distance of 6.4 mm. The sample tested was coated with a 2 nm layer of Au/Pd (Gold/Palladium) to ensure the conductivity of all samples.

The (wide angle) X-Ray Diffraction analysis was performed on powder obtained with air-dried neat NFC suspensions kept at ambient temperature (23°C) and relative humidity of 28.8%. The grafted samples are obtained by film casting evaporation and reducing the reslting film in powder form. The samples were placed in a 2,5mm deep cell and the measurements were performed with a PANanalytical, X'Pert PRO MPD diffractometer equipped with an X'celerator detector. The operating conditions for the refractometer were: Copper Kα radiation (1.5418 Å), 2θ (Bragg angle) between 5 and 60°, step size 0,067°, counting time 90s. The degree of crystallinity was evaluated using the Buschle-Diller and Zeronian (Buschle-Diller and Zeronian 1992) expression (Equation 1):

$$Ic = 1 - I1/I2 \qquad \text{Eq. 1}$$

Where: I_1 is the intensity at the minimum (2θ = 18°) and I_2 is the intensity associated with the crystalline region of cellulose (2θ = 22.5°). All the measurements were carried out at least in duplicates.

Infrared spectra were recorded on film for unmodified NFC or on powder form for modified NFC, using a Perkin-Elmer SP100 spectrometer. For each sample, the Diamond crystal of an attenuated total reflectance (ATR) apparatus was used. The torque applied was kept constant to ensure a same pressure on each sample. All spectra were recorded between 4000 and 600 cm^{-1}, with a resolution of 4 cm^{-1} and 8 scans. At least three different samples were tested and the most representative one were selected.

Contact angle measurements were carried out by depositing water droplets at the surface of the studied substrates and recording the angles formed using an OCA dataphysics system equipped with a CCD camera. The contact angle and the drop volume acquisition were realized during the first 60 seconds after deposition taking 4images/s. For unmodified NFC, the measurement was performed on dried film whereas for modified NFC, pellets were prepared and used. All measurements were performed at least 5 times for each sample and averaged.

1.2.6 Paper hand-sheet characterizations

In order to get retention values of the added NFC, white water or back water (water hand-sheet effluents) obtained during the vacuum filtration step of paper hand-sheets was collected and filtrated using a sieve with a mesh screen of 1µm in order to recover the non-retained NFC during the formation of the sheets and quantify them. The remaining NFC was placed in an oven at 105°C for five hours before being weighted. The retention rate has been calculated as follows (Equation 2):

$$Tr = 100 * (Ww - Wo)/Wa \qquad \text{Eq. 2}$$

Where: *Ww* is the mass weighted after filtration, *Wo* the mass of fibers that pass through the filter grid and *Wa* the theoretical mass of NFC added to the slurry.

Tensile properties were measured using a vertical testing machine (Lorentzen & Weltre) following the International standard *ISO 1924-2:2008*. The values are an average of at least 10 measurements performed on different paper sheets.

Air permeability was measured with a "Mariotte system" using a permeation cell of 2 cm² at room temperature (25°C and 50% RH) following the International standard ISO 5636-2:1984. The depression was imposed between 15 and 20 cm water column. Intrinsic permeability (K) was calculated following the Darcy's law (Equation 3):

$$Q = K * A * \Delta P/e\tau \qquad \text{Eq. 3}$$

Where: Q is the volume flow rate ($m^3.s^{-1}$), K the intrinsic permeability (m²), A the area tested (m²), ΔP the depression imposed (Pa), e the thickness (m) and τ the dynamic viscosity ($kg.m^{-1}.s^{-1}$).

Water absorption measurements, commonly named $Cobb_{60}$ tests, were performed using a ring of 10 cm² and all samples were cut around the ring in order to avoid errors associated with the capillarity. 10 mL of deionized water was added into the ring for 60 seconds, following the International standard *ISO 535*. Then, "wet samples" were pressed once between two absorbent papers with a roll of 10 kg in order to remove residual water and weighted with a four digit balance. Following the same procedure, $Cobb_{600}$ and $Cobb_{1800}$ were performed on papers reinforced with neat and modified NFC after the contact with water for 600s and 1800s, respectively.

Cross-section and surface of hand-sheets were investigated using a FEI-Quanta 200 Environmental Scanning Electron Microscope (ESEM). The accelerating voltage (EHT) was 10kV for a working distance of 10 mm. The samples were coated with a layer of Au/Pd (Gold/Palladium) and an Everhart Thornley Detector (EDT) was used.

1.3 Results and discussions

1.3.1 NFCs characterizations

Neat NFC and modified NFC were first produced and then characterized thanks to the FE-SEM technique, as shown in the Figure 1-2, both nanofibrillated cellulose display fibrillar structure with a diameter around 23nm ± 7nm and 31 ± 8 nm for neat and modified NFC respectively. The diameter of nanofibrillated cellulose was determined by digital image analysis (ImageJ) of FE-SEM pictures (a minimum of 50 measurements was performed).

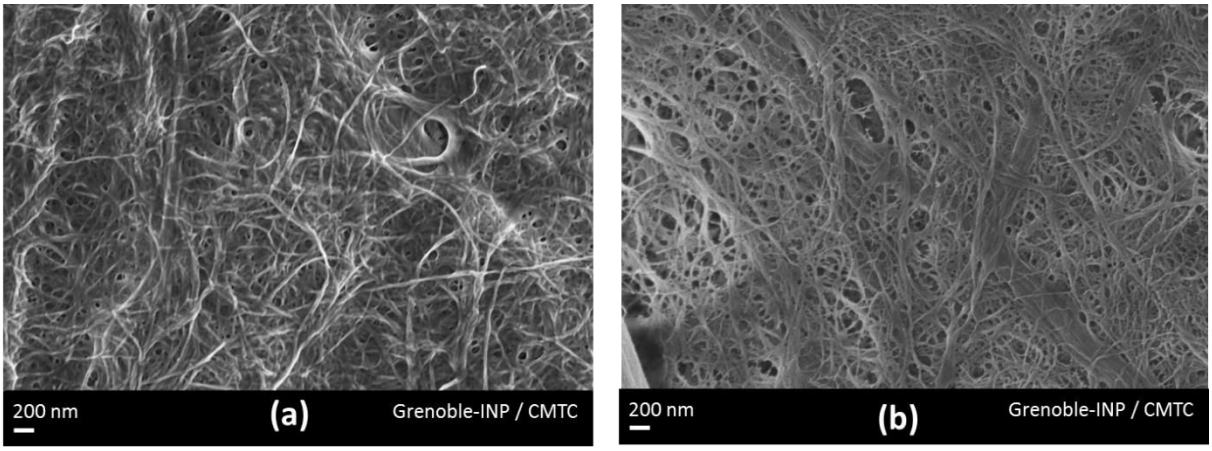

Figure 1-2 : FE-SEM pictures of (a) Neat NFC) and (b) modified NFC with nanoemulsion

The micrograph shows that neat NFCs are strongly entangled and packed together whereas the network of modified NFCs seems to be more porous, showing that probably less hydrogen bond interactions between modified NFC. The FE-SEM micrographs indicate that the morphology and the nano-scale are conserved.

The crystalline structure of neat and grafted NFCs has also been investigated by XRD (data not shown). The crystallinity indices of the reference sample (80.2%) and that of the grafted counterpart (78.3%) were found to be similar. This confirms that there is no alteration of crystalline part of NFC during the chemical modification even in these swelling conditions.

Chemical grafting between NFC and nanofibrillated cellulose have been investigated by FTIR and Contact angle measurements. Figure 1-3 shows FTIR spectra of both samples (i.e. neat NFC and modified NFC) and displays some similar characteristic bands attributed to cellulose substrates. Thus, the bands around 3496cm^{-1} (O–H), 1110cm^{-1} (C–O of secondary alcohol) (used for the normalization of all spectra) and 2868 and 2970cm^{-1} (C–H from –CH_2–) are detected and identified.

After the esterification reaction, a characteristic peak assigned to ester bonds between 1720–1750cm^{-1} has clearly appeared. Moreover, a strong increase of the bands at 2868 and

2970cm^{-1} corresponding to asymmetric and symmetric –CH_2 – stretches from aliphatic chain of AKD is also observed. So, FTIR measurements show some changes in the chemistry of grafted NFC, thus proving that the cellulose surface has most probably been modified.

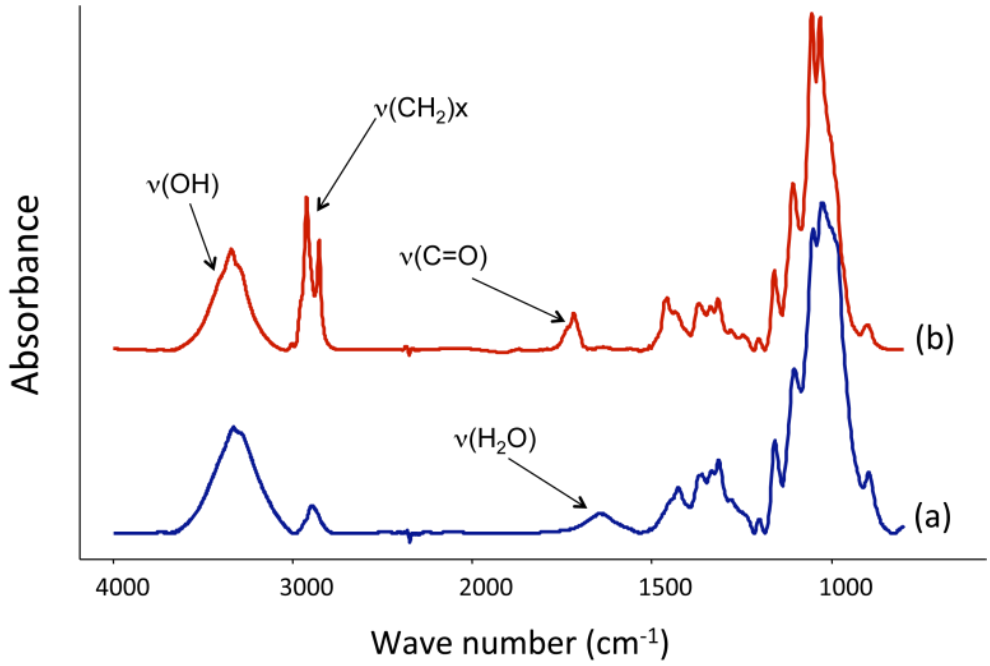

Figure 1-3 : Fourier Transformed Infra-Red spectra for (a) neat NFC and (b) modified NFC

In addition, contact angle measurements were performed in order to point out the hydrophobic behavior of the grafted nanofibers comparing to neat NFC (results not shown). As expected the contact angle values of a drop of water deposited on the surface of the grafted NFC are higher than those found for the neat NFC. The neat NFC displayed a decrease of the contact angle value with the time and vanished at 20°. The initial values are 56° and 105.8° for neat and grafted NFC, respectively. The value of the grafted samples is stable during the acquisition and they are higher than those found for neat NFC surface, proving indirectly the chemical grafting.

In conclusion, thanks to Infra-Red and contact angles measurements, the NFC seems to be grafted. The purpose of this paper is not focused on the chemical grafting, that is why no further characterization will be made. Thus, the major study concerns the effect of the modified NFC on the fiber based material properties.

1.3.2 Retention characterization

Sheets of paper were reinforced following two strategies as sketched in Figure 1-4 Sheets were filled with 5, 10, 20, 30 and 50% of neat and chemically modified NFC

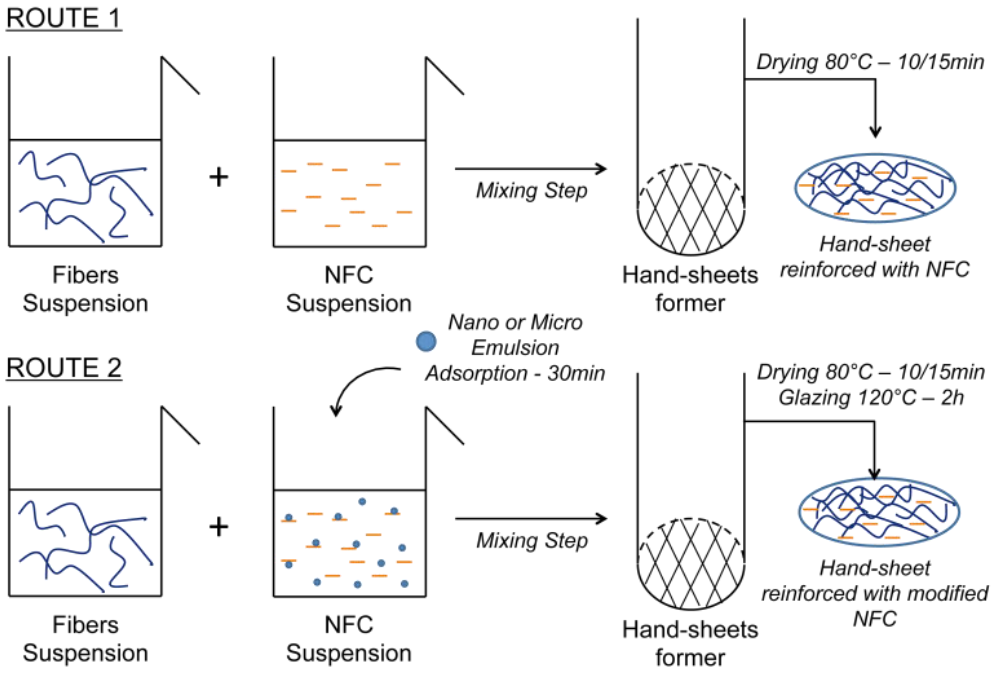

Figure 1-4 : Strategies followed to obtain fibers based materials reinforced with (route 1) neat NFC and (route 2) modified NFC

Retention values of added NFC were measured after filtration of "*white water*" obtained during the preparation of hand-sheets. In order to avoid the influence of fiber suspension on retention values, it has been chosen to work at a constant concentration of 2g/L of fibers and NFC. Results are presented in the Figure 1-5.

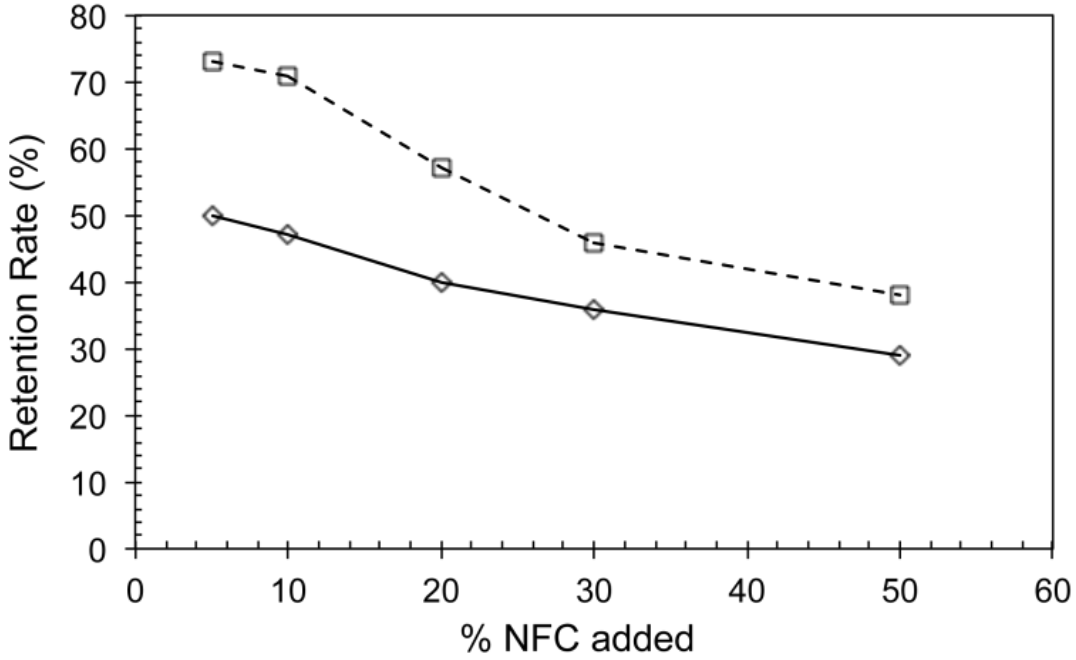

Figure 1-5 : Retention value obtained for neat NFC (solid line) and modified NFC (dotted line)

Although NFC exhibits lower dimensions than those of the filtration wire mesh, a certain amount of them was retained in the bulk. The retention of NFC can be explained by several effects: (i) clogging caused by the fiber suspension, (ii) entanglement of NFC and (iii) interactions phenomena. As discussed previously, NFC display high hydroxyl content at their surface, so they can easily form hydrogen bonds with each other but also with fibers. Moreover cellulose nanofibrils present a high aspect ratio and a web-like structure, so they can also be easily entangled within the fibrous network. For both neat and modified NFC, the retention value decreases with the added amount of NFC. Beyond a given concentration, the fibrous network is already structured and closed, so it becomes difficult for nanofibrils to be adsorbed within the fiber network. Moreover, higher is the quantity of added NFC; bigger is the probability to pass through the filtration wire (Table 1-1).

Table 1-1 : NFC retention value for all percentage of NFC theoretically added in pulp slurry

NFC added (%)	Mass of NFC in sheets (g)	Retention for NFC (%)	Retention for modified NFC (%)
5	0.1	73	50
10	0.2	71	47
20	0.4	57	40
30	0.6	46	36
50	1	38	29

It might be due to the lower quantity of fiber when increasing quantity of NFC as the total amount of NFC and Fiber is constant. This limits clogging and adsorption effect; but a difference between chemically grafted and neat NFC is noticed. Thus, all future graphs will be presented with the real amount of NFC retained in the hand-sheets.

1.3.3 Structural characterization

Figure 1-6 shows surface of (a) reference paper, (b) paper reinforced with 50% of Neat NFC and (c) paper reinforced with 50% of modified NFC. At this stage, the difference between treated and untreated paper is clearly observed. In fact, for the paper reinforced with 50% of NFC or with 50% of modified NFC, the fibers seem to be more packed together thanks to the nanofibrils acting as a binder in paper.

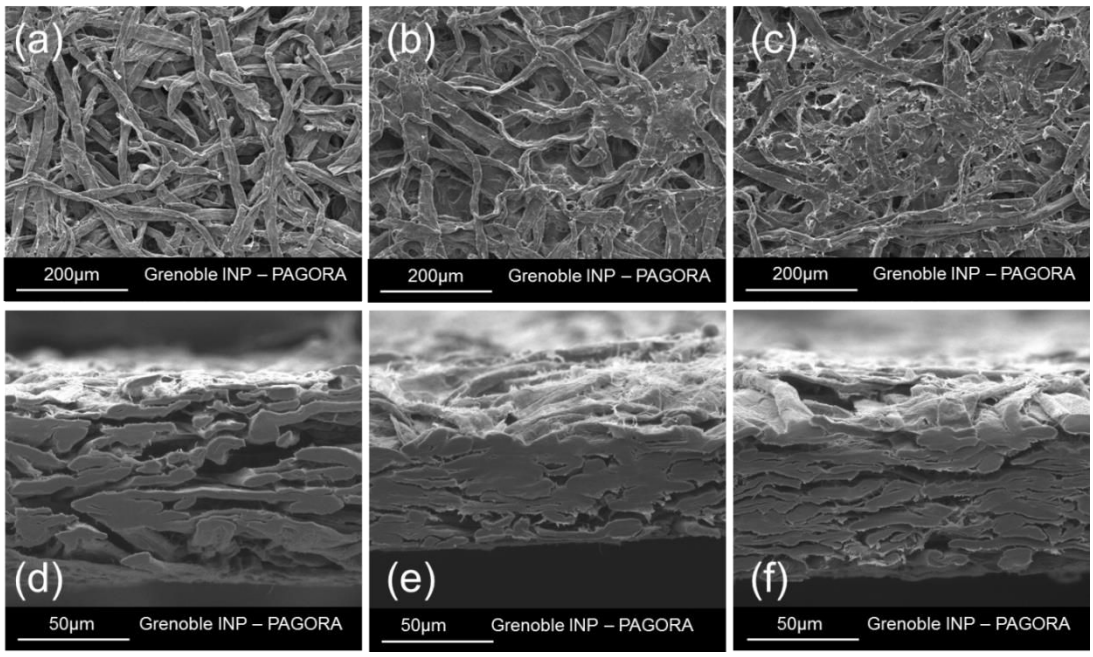

Figure 1-6 : SEM images of surface paper reinforced (a) without NFC (reference), (b) with NFC, (c) with modified NFC and cross section of (d) without NFC, (e) with NFC and (f) with modified NFC

The porosity seems to be lower in the hand-sheet filled with both neat and modified NFC. However, NFCs seems to be not homogeneously deposited at the paper surface but rather within the material and some aggregates can also be observed. Moreover, cross sections of these samples were investigated and show that the fibrous network was clearly more closed and dense for paper reinforced with both NFCs in comparison to the reference paper. Therefore, papers filled with neat NFC are denser resulting from a better absorption of neat NFC onto fibers. Such density measurements were performed and confirmed this assumption as shown in Figure 1-7.

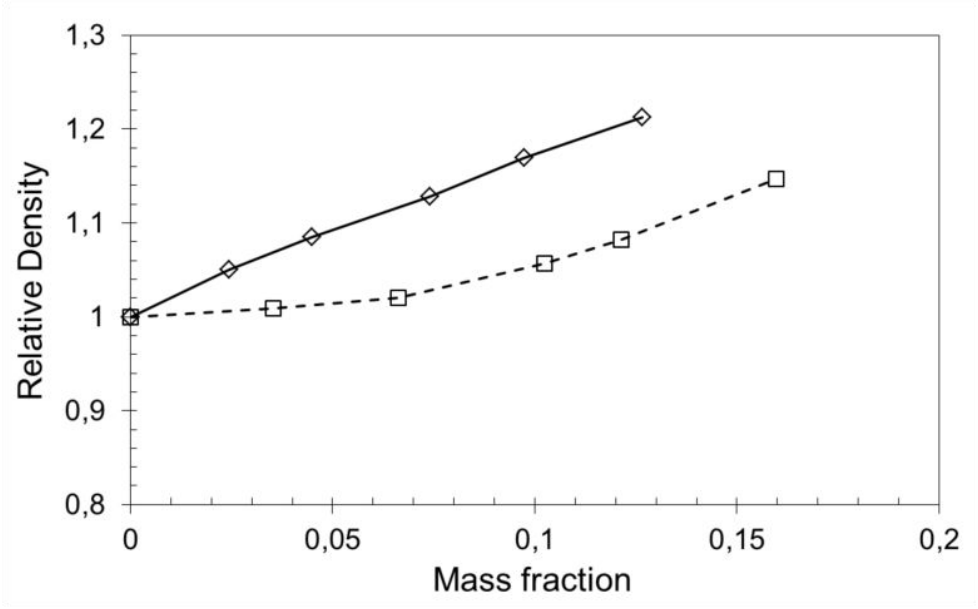

Figure 1-7 : Relative density for neat NFC (solid line) and modified NFC (dotted line)

As presented in the Figure 1-7, sheets prepared with NFC are denser than those corresponding to modified NFC-filled papers. For the higher content of NFC, the density increases up to 20% and 15% for neat and modified NFC, respectively. This observation is comparable to a refining step in pulp and paper industry. Indeed higher refining gives higher densities. However it was proved in SUNPAP workshop that for such pulps (i.e. bleached softwood), the reinforcement effect at equivalent Schopper degree is much more efficient with NFC than refining process (Hamann 2011).

1.3.4 Tensile and barrier properties of hand-sheets

Figure 1-8 presents the mechanical properties of hand-sheets reinforced with both neat and modified NFC. The conclusions are the same whatever the investigated properties: the mechanical properties are better for papers reinforced with neat or grafted NFC. Indeed, with only 12 %wt. of NFC the Young's modulus and the breaking length values have more than doubled. With modified NFC the improvement is more modest. With 16 %wt. of modified NFC, Young's modulus and breaking length increase by 72 and 51%, respectively. Such results are in accordance with literature. (Eriksen and Syverud 2008)

As shown before, the paper samples containing NFC (modified or not) have higher densities compared to reference material. This can explain, only partly, such an increase. Indeed, if these values are normalized with respect to the density (they are divided by density values), then the same tendencies are obtained as shown in Figure 1-8, which indicates that an additional reinforcement effect due to NFC contribution, even for modified NFC.

The reinforcing effect provided by the addition of nanofibrillated cellulose does not involve a decrease of the elongation at break, as shown in the Figure 1-8. This, predicts, that, contrary to composites, the fiber based material is still flexible. Due to the addition of cellulosic nanofibers, interactions are stronger and the fibrous network keeps its elasticity. As said before, NFCs exhibit a high aspect ratio and a web like structure, providing a highly elastic behavior to papers. The slight evolution of elongation might be also due to the change of density.

In conclusion, after the sizing the interaction between grafted NFC (hydrophobic) and the fiber networks (hydrophilic) are slightly lower but still enough to improve mechanical properties.

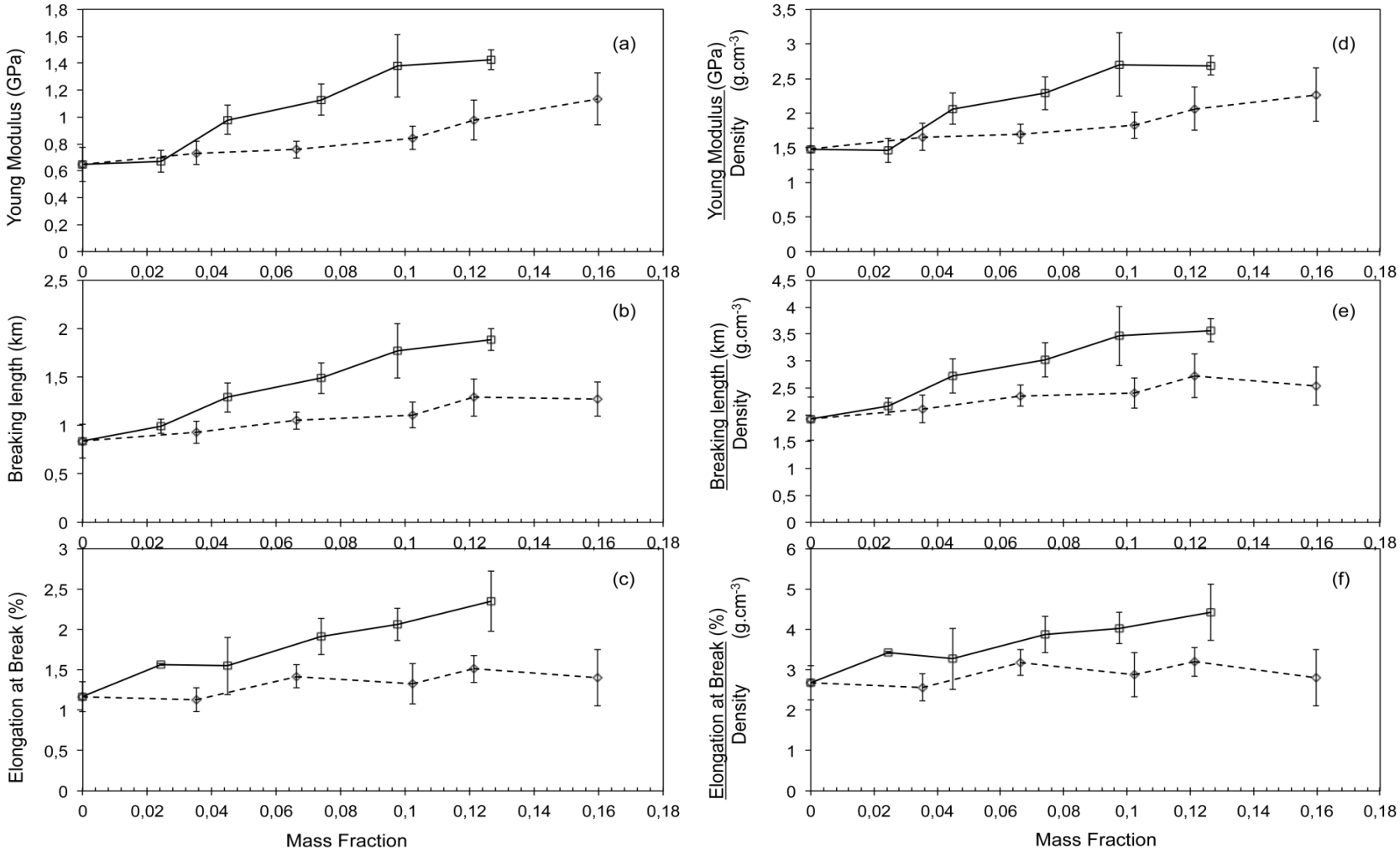

Figure 1-8 : Mechanical properties of paper sheets reinforced with neat NFC (solid line) and modified NFC (dotted line) / (a) Young modulus (b) Breaking length (c) Elongation at break / (d) Young modulus divided by density obtained for each samples, (e) Breaking length divided by density and (f) Elongation at break divided by density

As recently described (Syverud and Stenius 2009), NFC is a good candidate to improve gas barrier properties of papers thanks to the formed nanoporous network. In this context, air permeability has been investigated and compared using neat and modified NFC.

Air permeability of paper sheets was measured on both sides. Figure 1-9 shows the air permeability measurements as function of added amount of cellulosic nanofillers. In order to avoid errors related to the thickness and the basis weight of papers obtained, it has been decided to focus our study on the intrinsic permeability so called K, which depends only on the structural properties of materials. Indeed, K parameter depends on both the porosity and the specific surface area of fibrous network. Papers with high porosity are in general more permeable, on the contrary permeability decreases as the specific surface area increases. As expected, the air permeability of papers decreases with the addition of neat and modified NFC. It is worth to note that the density of paper sheets increases with the amount of nanofibrillated cellulose, which yields a more closed mat (as already presented in Figure 1-7). Consequently, it is harder for the fluid to pass through the fibrous network. Moreover, due to their nano-scale dimension and their web-like structure, NFC increases significantly the internal specific surface area of materials decreasing by the same way the permeability. This is the reason why, there is no significant difference between papers willed with neat and treated NFC.

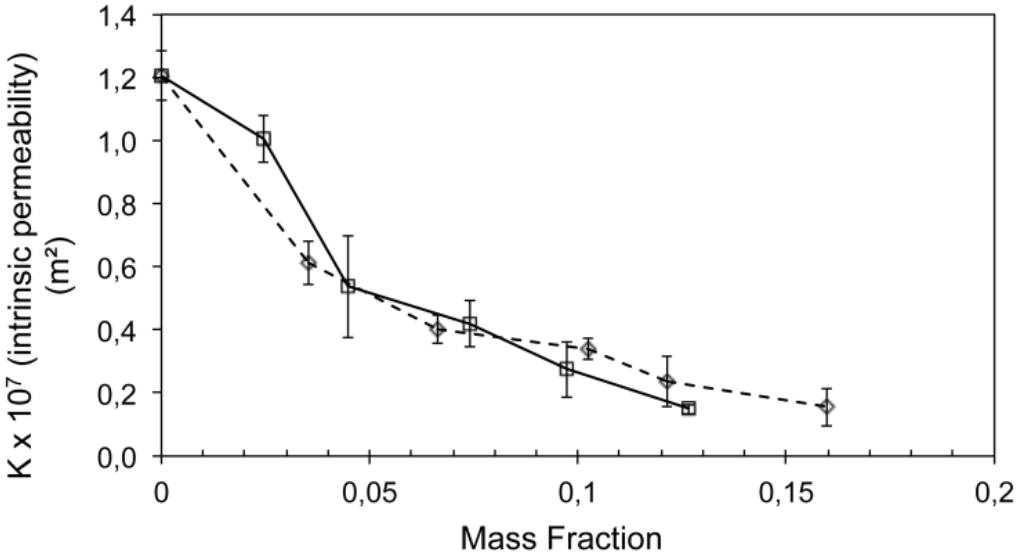

Figure 1-9 : Intrinsic permeability for neat NFC (solid line) and modified NFC (dotted line)

Moreover, the air permeability was significantly the same for both sides (not shown) reflecting a homogenized distribution of nanofibrillated cellulose within the paper hand-sheets.

1.3.5 Sizing effect on water sorption

As previously mentioned AKD is well known to impart hydrophobic properties of treated papers, the so called the sizing effect. The Cobb value is commonly proposed as a comparative study. Indeed classically untreated paper sheets of 80-120 g/m² display a $Cobb_{60}$ around 100 g/m², meaning water absorption of paper is high and correspond to 100g/m². Figure 1-10 shows Cobb values as a function of added amount of NFC. As expected no positive influence was observed for neat NFC. On the contrary, results obtained for papers reinforced with modified NFC are very interesting. Indeed, a strong decrease of Cobb values was observed with low contents of modified NFC. Cobb values of papers reinforced with 3.5%wt. modified NFC display a decrease of 81%. Indeed with a very low quantity of modified NFC introduced in paper sheets (theoretical value: 5% wt., which correspond to 0.4 %wt. of sheets), the Cobb value decreases from 97 to 15. This behavior was attributed to hydrophobic nature provided by AKD attached to NFC.

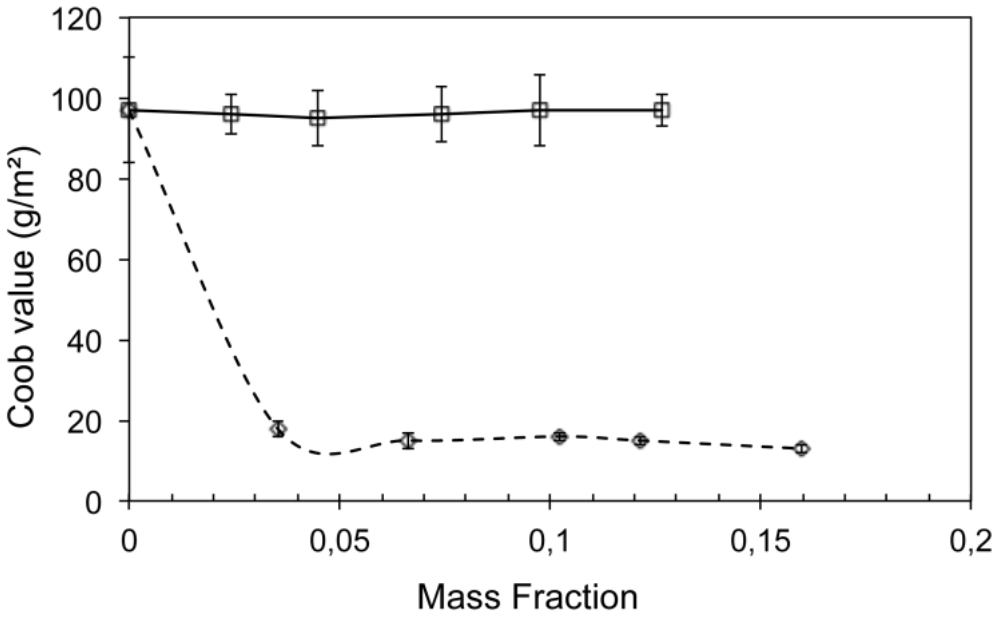

Figure 1-10 : Cobb value obtained for neat NFC (solid line) and modified NFC (dotted line)

In order to confirm this characteristic, $Cobb_{600}$ and $Cobb_{1800}$ were performed. As presented in the Table 1-2, even if the contact between water and the treated surface is longer, the treated paper, keep its hydrophobic character.

Table 1-2. Influence of water contact time on sheets reinforced with modified NFC during 60, 600 and 1800 seconds

Modified NFC added th. (%)	$Cobb_{60}$ (g/m²)	$Cobb_{600}$ (g/m²)	$Cobb_{1800}$ (g/m²)
0	97 ± 13	97	97
5	18 ± 2	23 ± 1	29 ± 1
10	15 ± 2	18 ± 1	25 ± 2
20	16 ± 1	18 ± 2	25 ± 1
30	15 ± 1	19 ± 1	25 ± 1
50	13 ± 1	20 ± 2	25 ± 2

Moreover, contact angle measurements (data not shown) were performed with water to confirm this behavior. Indeed, because of the high water absorption of untreated NFC papers, no water contact angles could be measured. On the contrary, paper reinforced with modified NFC has water contact angle values of about 100° ± 3°.

In conclusion, a strong effect can be observed when hand sheets were made with NFC previously treated with AKD nanoemulsion. A comparison with classical AKD emulsion treated paper is proposed in the following part of this study.

To point out the benefit of NFC and nanoemulsions in comparison to classical emulsions of AKD, some tests were performed with Aquapel emulsion (5% wt.) which contains 30% of AKD. Table 1-3 shows clearly that the internal sizing of nanoemulsion treated NFC is as efficient as Aquapel emulsions (referred as AKD). However, as discussed before, hand-sheets paper reinforced with both NFC (neat and modified) improve also strongly the mechanical and decrease drastically the air permeability even if the NFCs are modified.

Table 1-3. Sum-up of mechanical properties, air permeability and sizing effect of Reference paper, paper treated with AKD microemulsion, paper reinforced with 12%wt. of neat and modified NFC

	Reference Paper	Treated Paper (AKD	Neat NFC (30%)	Modified NFC (30%)
Mechanical Properties				
Density ($kg.m^{-3}$)	455 ± 18	456 ± 7	511 ± 15	473 ± 9
Young's Modulus (Gpa)	0.65 ± 0.03	0.78 ± 0.08	1.38 ± 0.24	0.98 ± 0.15
Breaking Length (Km)	0.84 ± 0.18	0.90 ± 0.14	1.77 ± 0.28	1.29 ± 0.19
Elongation at Break (%)	1.17 ± 0.23	0.97 ± 0.23	2.06 ± 0.20	1.51 ± 0.17
Air Permeability Measurements				
K (m^2)	1.22E-07 ± 8.02E-08	1.16E-07 ± 1.35E-08	2.75E-08 ± 0.9E-08	2.35E-08 ± 0.8E-08
Water Absorption				
$Cobb_{60}$ ($g.m^{-2}$)	96 ± 13	11 ± 1	97 ± 9	15 ± 1
$Cobb_{600}$ ($g.m^{-2}$)	/	15 ± 2	/	19 ± 1
$Cobb_{1800}$ ($g.m^{-2}$)	/	22 ± 2	/	25 ± 1

1.4 Conclusions

The nanocelluloses can be used in several fields and some scientific papers have already reported the benefit of NFC in fiber based materials like paper sheets. But, to best of our knowledge, modified NFCs were never used in paper. In this study, treated NFC impart 2 different properties i.e. mechanical and barrier reinforcements but also an internal sizing of paper. Cobb values for sized paper commonly reached in industry correspond to those obtain in this study. The air permeability is strongly decreased and mechanical properties strongly improved comparing to industrial material. The synergy of such properties is very difficult to achieve and this new strategy opens the field of several application like barrier material or filtration.

Acknowledgments

This research was supported by the "Scale-Up of Nanoparticles in modern PAPermaking" (SUNPAP) project of the seven framework program of European research. Authors want to thanks José Garrido-Garcia, Bertine Khelifi and Stéphane Dufreney from LGP2 (France) for their technical supports in this research.

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2. All-Cellulose bionanocomposites: cellulose derivatives reinforced with chemically modified nanofibrillated cellulose

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Abstract

Bionanocomposites based on different types of nanofibrillated cellulose (NFC) and cellulose ester derivatives were prepared using film casting methods. Chemical surface modification was performed on the surface of NFC reinforcing elements and five different matrices were tested. The idea was to create similar cellulose derivatives at the surface of NFC in order to have "continuous" interface. FE-SEM, water uptake and TGA were performed to understand bionanocomposite morphology and structure. Dynamic mechanical thermal analyses demonstrated that significant improvements in the thermomechanical properties of the bionanocomposites were achieved when neat NFCs were added. The addition of cellulosic nanofillers at 10%wt. increases considerably the length of the rubbery plateau, thus allowing the extension of the range of use of the ensuing materials. The chemical modification seems not improving more the reinforcement (compromise between compatibility and NFC network stiffness) but keeps the reinforcement and modifies the film structure.

Keywords

Nano-structures, Polymer-matrix composites, Thermomechanical properties, Surface treatments

***Inspired from**: Karim Missoum, Naceur Belgacem, Florian Martoïa, Julien Bras – Composite Part A: Applied Science and Manufacturing (2012) – Submitted*

2.1 Introduction

Cellulose is the most abundant renewable polymer with an annual worldwide production estimated to be between 10^{10} and 10^{11} tons each year. Cellulose fiber based composites are widely spread in our society and used in several industries like automotive, aero-space, packaging etc. Several reviews dealing with these applications, and describing the surface treatments of the reinforcing phase, as well as the properties of the obtained composites are available in the literature (Bledzki and Gassan 1999; Eichhorn et al. 2001; Belgacem and Gandini 2008). Such cellulosic composite fillers have several advantages (i.e renewable, biodegradable, cost effective, light and able to burn when incinerated) but some compatibility issues might occur with the classical non-polar polymer classically used. Since 30 years, there is meanwhile a growing interest in nano-scaled filler within composite industry. For these two reasons, cellulose-based nanoparticles have been more and more investigated for nanocomposite applications since mid of 90's. Two kinds of cellulose nanoparticles can be obtained from cellulosic fibers depending on the applied treatment , as summarized in several reviews devoted to: (i) NanoCrystalline Cellulose (NCC)(Azizi Samir et al. 2005; Habibi et al. 2010; Lin et al. 2012) obtained by a strong acid hydrolysis of cellulose fibers and (ii) NanoFibrillated Cellulose (NFC)(Eichhorn et al. 2010; Siró and Plackett 2010a) produced applying mechanical treatment under a high pressure. This study will focus on the second type of nanocellulose: the NFCs. In comparison to NCC, which are rigid and displaying a rod-like structure, NFCs can be described as a long and flexible cellulosic material, with a diameter ranging from 20 to 50 nm and a length of several micrometers. Due to their stiffness and their nano-scale size, they display high specific area which provides them strong reinforcement ability at low concentration within a matrix. This reinforcement is even enhanced with their ability to establish hydrogen bonds. In 1983, Turbak et al.(Turbak et al. 1983) have discovered NFCs and only about 25 years later, they started to be exploited in such applications with exponential increase of scientific paper. Their uses as reinforcement in nanocomposite has been recently reviewed (Siqueira et al. 2010b) and some astonishing reinforcement's effect has already been achieved. Due to the good stability of cellulose nanofibrillated cellulose in water, the mixing of hydrosoluble polymers (e.g. cellulose ethers) or latex emulsion (e.g. Natural Rubber) with NFC and subsequent film casting has been the preferred method to produce polymer-NFC nanocomposites(Johnson et al. 2009; Eyholzer et al. 2010; Zimmermann et al. 2010; Sehaqui et al. 2011; Bilbao-Sainz et al. 2011). The development of the processing technologies in which non-aqueous polymers are used as a matrix is one of the biggest challenges today and in the near future. In order to improve the dispersion of NFC in non-aqueous solvent and, which also help their good dispersion in

hydrophobic matrix, several strategies have been adopted, including the use of surfactants and chemical modifications of their surface hydroxyl groups(Siqueira et al. 2009; Rodionova et al. 2010; Siqueira et al. 2010a; Lonnberg et al. 2011; Filpponen et al. 2012; Missoum et al. 2012a). Less than 50 papers all around the world dealt with the strategy concerning chemical surface modification of NFC and only few of them was applied in composite area. Nevertheless, first studies with PCL (Siqueira et al. 2011a) or PLA (Goffin et al. 2011) are promising for example.

The innovative idea of this study is to carry on improving interface between NFC and the matrix by creating cellulose derivatives at the surface of NFC which will be exactly the same (or very similar) than the matrix. In this case, we should have a continuum interface between matrix and NFC and achieve a 100% cellulosic material which presents several advantages. Only one scientific paper from Siqueira et al. (Siqueira et al. 2011b) has dealt with this strategy but with cellulose nanocrystals which behave differently and can be subjected to the pealing effect. Lu et al. (Lu and Drzal 2010) reported the feasibility of nanocomposites using chemically modified NFC and Cellulose Acetate (CA) as a matrix. This study deals with comparing neat and silylated NFC in cellulose ester derivatives matrix. The authors concluded that both DMA and tensile tests showed the good reinforcing effect of NFC, especially with silanes treated NFC, which results in better dispersion with the polymer matrix. However in this case, the cellulose modification was quite different than the matrix.

In the present study, several cellulose ester derivative matrices and neat/modified NFCs have been considered to perform bionanocomposites originating from cellulosic materials. The target of this study was to check the benefit of neat and chemically modified NFC in reinforcing several cellulose derivatives matrices. The main idea was to produce “all cellulose bionanocomposites” by casting. To the best of our knowledge, such study is conducted for the first time.

2.2 Experimental

2.2.1 Materials

The wood pulp was kindly delivered by Domsjö (Sweden) and corresponded to a mix between Spruce and Pine (60% and 40%, respectively). This material is a dissolving pulp referred to sodium based sulfite mill extraction and used for the production of NFC. Endoglucanase used for the cellulose fibers pretreatment was purchased from Novozyme (Denmark).

For chemical modification of NFC, all the reagents and solvents (acetic, butyric, iso-butyric, hexanoic anhydride, the ionic liquid [bmim][PF6], ethanol, acetone and dichloromethane) were purchased from Aldrich and co. (France) . They were high purity reagent grade and used as received without further purification. Deionized water was used in all experiments.

Cellulose Acetate Butyrate (CAB), Cellulose Acetate Propionate (CAP) and Carboxymethyl Cellulose Acetate Butyrate (CMCAB) were provided by Eastman ® Chemical Company (USA), to whom we are indebted.

Each cellulose ester matrices were analyzed by liquid ^{13}C NMR. Sample tests were prepared by dissolving 100 mg of cellulose ester in 8 mL of DMSO-d6. The solution was then stirred for at least two hours to ensure complete dissolution of macromolecular chains. Quantitative Carbon ^{13}C NMR was carried out with a probe 10mmBB for 12 hours. Quantitative Carbon ^{13}CNMR analyses were conducted in the Institute of Nanoscience and Cryogenics (INAC) to the Atomic Energy Center (CEA) in Grenoble. Spectra were recorded at 50°C, on a UNITY400 (Varian) spectrometer. Experiments were performed with a 10 mm BB (Broad Band) probe. The data were acquired and processed with VNMR version 6.1b VARIAN software on SUN station with Solaris OS system. The position of the peaks are given relative to TMS (tetramethylsilane δ = 0 ppm), and are referenced with the residual solvent signal, DMSO-d6 (δDMSO= 39, 5 ppm).Quantitative ^{13}C spectra were obtained at 100,580 MHz with usual one pulse sequence with broadband proton decoupling only during the acquisition time to avoid nOe (nuclear Overhauser effect), with 25 kHz spectral width, 0.48 s acquisition time, 11 s relaxation delay, 45° pulse.64 K zero-filling, 4 Hz line broadening was applied before Fourier Transform.24 hours of acquisition are required to obtain a usable ^{13}C spectrum. The degree of substitution was obtained by integrating peaks. Integration values were then normalized to the value given by the peak of the carbon C1 of the cellulose at 101.76 ppm.

2.2.2 Neat and modified NFC preparation and characterization

Nanofibrillated cellulose suspension was produced from Domsjö pulp. A suspension of bleached Domsjö fibers (2.0%wt.) was enzymatically pretreated with endoglucanase (Cellulase) during 1h at 50°C. Then, the resulting slurry was fibrillated using a Masuko Grinder© (Japan). Size reduction of the fibers into nanofibrillated cellulose was obtained after 10 passes between the rotating and the static stones at 1,500 rpm. Solid content of the NFC suspensions was around 2.6% (w/w).

Four grades of modified NFC were obtained using acetic, butyric, iso-butyric and hexanoic anhydride within ionic liquid solvents. The method used for the surface modification of NFC in ionic liquid was presented and detailed in a previous paper (Missoum et al. 2012a).

FE-SEM, model Zeiss Ultra column 55 gemini, was used for the characterization and the determination of NFC's diameter. The accelerating voltage (EHT) was 3 kV for a working distance of 6.4 mm. One drop of dilute suspension of modified NFC was deposited on a substrate covered with carbon tape. After drying of samples, they were coated with a 2 nm layer of Au/Pd (Gold/Palladium) to ensure the conductivity of all samples.

Contact angle measurements were carried out with water droplets deposited at the surface of the studied substrates and recording the formed angles, using an OCA dataphysics system equipped with a CCD camera. Acquisitions were realized during the first 60 seconds after deposition, taking 50 pictures/s. For both modified and unmodified NFC, the measurement was performed on pellets and dried films respectively. All the measurements were performed 7 times for each sample and averaged.

2.2.3 Bionanocomposite films preparation

A cellulose acetate solution (≈10%wt.) was prepared by dissolving 1g of the polymer matrix in 10g of acetone. The solution was stirred for two hours to ensure the complete dissolution of the polymer. Then, a suspension of neat and modified NFC was prepared at about 5%wt by dispersing the different type of NFC in acetone after a solvent exchange procedure, i.e. several steps of centrifugation at 10000 rpm and re-dispersion in acetone using Ultra-Turrax T25 device. NFC suspensions in acetone were mixed during two hours with the appropriate amounts of cellulose acetate solution to reach a content of 2.5, 10, 23%wt. with respect to nanofiber loadings. The previous mixture was then casted into Teflon molds and covered with a perforated box, in order to control the acetone evaporation rate, thus obtaining planar films without the presence of any cult. Casted films were then dried under vacuum at room temperature for at least 1 hour, in order to remove the remaining acetone.

2.2.4 Characterizations of bionanocomposites

Dynamic Scattering Calorimetry (DSC) experiments were carried out with a DSC Q100 differential calorimeter (TA Instruments) fitted with a manual liquid nitrogen cooling system. The samples were placed in hermetically closed DSC capsules. The heating and cooling rates were 10 °C min^{-1} and under N_2 atmosphere. Sample weights were between 5 mg and 15 mg. All samples were analyzed at least three times and averaged. All measurements were reproducible and present a standard deviation of 1-2°C.

Dynamical mechanical analysis (DMA) of the nanocomposite films was performed using RSA3 (TA Instruments) equipment working in tensile mode. Data acquisition was carried out with the software TA Orchestrator 7.0. The measurements were carried out at a constant frequency of 1 Hz, strain amplitude of 0.05% and in the temperature range of 35°C to 340°C. The used gauge length was 10 mm, whereas the sample width and thickness varied from 5 to 6 mm and 0.08 to 0.3 mm, respectively. The reported results are an average based on at least three samples.

Water Uptake measurements were performed on films. The specimens used were thin rectangular strips with dimensions of 20mm x 8mm x 0.15mm. The films were therefore supposed to be thin enough for the molecular diffusion to be considered mono-dimensional. Samples were first dried overnight at 105°C. After weighting, they were immersed in deionized water.

They were then withdrawn periodically, and weighted using a four-digit balance. The water content or water uptake of the samples was calculated as follows:

$$\text{Water Uptake (\%)} = (Mt-Mo)*100/Mo \qquad \text{Eq. 1}$$

Where: Mt and Mo are the weights at time t and before immersion in water. Mo corresponds therefore to the weight of dry solid, determined after drying overnight at 105°C. The mean moisture uptake of each sample was calculated at various conditioning times (t) with at least duplicates.

Cross-section and surface of bionanocomposites were investigated using a scanning electron microscope equipped with a field emission gun (FE-SEM), model Zeiss Ultra column 55 Gemini. The accelerating voltage (EHT) was 5 kV for a working distance of 10 mm. Pieces of films were scratched onto a substrate covered with carbon tape and then coated with a 2 nm layer of Au/Pd (Gold/Palladium) to ensure the conductivity of all samples.

Thermogravimetric analysis (TGA) was performed using a TGA 2980 (TA instruments) from 30 to 600°C at a heating rate of 10°C/min under a flow of nitrogen of about 20mL/min. Approximately 15 to 20 mg of sample was used. The reported results are an average of two samples.

2.3 Results and discussions

2.3.1 NFCs characterizations

Neat and modified NFCs (i.e. NFC_AA, NFC_BA and NFC_HA corresponding to acetic-, butyric- and hexanoic anhydride-modified NFCs, respectively) were first produced and then characterized thanks to the FE-SEM technique. Their diameter dimensions were very similar with 36 ± 12 nm, 40 ± 16 nm, 55 ± 18 nm and 54 ± 15 nm respectively for NFC, NFC_AA, NFC_BA, NFC_HA.

We have already shown in the previous study (Missoum et al. 2012a) that, thanks to this ionic liquid strategy, NFC are chemically grafted only at the surface, achieving several characterization methods (i.e. Infra-Red, contact angle, Elemental analysis, XPS, SIMS…). In fact, it was clearly proved thanks to XPS and ToF-SIMS analyses that the grafting is occurred mainly at the surface, which displayed hydrophobic properties in comparison to those associated to neat NFC. Contact angle measurements were performed in order to point out the hydrophobic behavior of the grafted nanofibers (after Soxhlet washing), as presented in Table 2-1.

Table 2-1 : Contact angle value obtained of a water droplet for Neat NFC and modified NFC

	Contact angle values
Neat NFC	20°
NFC_AA	56° +/- 1
NFC_BA	98.6° +/- 1
NFC_HA	104.8° +/- 0.7

As expected the contact angle values of a drop of water deposited on the surface of the grafted NFC are higher than those found for the neat NFC.

The neat NFC displayed a decrease of the contact angle value with the time and vanished at 20°. The values of the grafted samples are stable during the acquisition and they are higher than those found for neat NFC surface with an increase link to the aliphatic chain of the grafted moiety, namely: 56°, 98.6°, 99.5° and 104.8° for acetic, butyric, isobutyric and hexanoic anhydrides treated NFC, respectively. A clear difference should be observed at the interface with the matrix depending on the chemical grafting.

2.3.2 Influence of cellulosic matrices

Before any composites forming, the degree of substitution of the commercial matrices was determined by ^{13}C NMR. Values obtained are presented in Table 2-2 for the three matrices after treatment of ^{13}C NMR spectra.

Table 2-2 : Degree of substitution of matrices obtained from ^{13}C NMR quantification.

Sample Name	CarboxyMethyl	Acetyl	Butyryl	Propionyl
CAB	---	1.02	1.67	---
CAP	---	0.1	---	2.60
CMCAB	0.41	0.09	1.88	---

CAB and CAP matrices displayed a DS value close to 2.7. For CAB matrix, half of modified hydroxyl groups are acetyl groups and other –OH groups were substituted in butyryl groups. Concerning CAP matrix, the major part of the modified hydroxyl group are propionyl groups (around 95%). In comparison, the CMCAB matrix displayed carboxymethyl, acetyl and butyryl functions. The last cited groups are the most present is this matrix. This characterization gives some worth information for the next part of the paper such as compatibility and interaction between neat and modified NFC and matrices.

Then, all bionanocomposites films were produced using a casting/evaporation technique, as presented in Figure 2-1. Three matrices, cellulose acetate butyrate (CAB), cellulose acetate propionate (CAP) and carboxymethyl cellulose acetate butyrate (CMCAB) were initially chosen in order to study the influence of the polymer matrix on the properties of nanocomposites and interfaces.

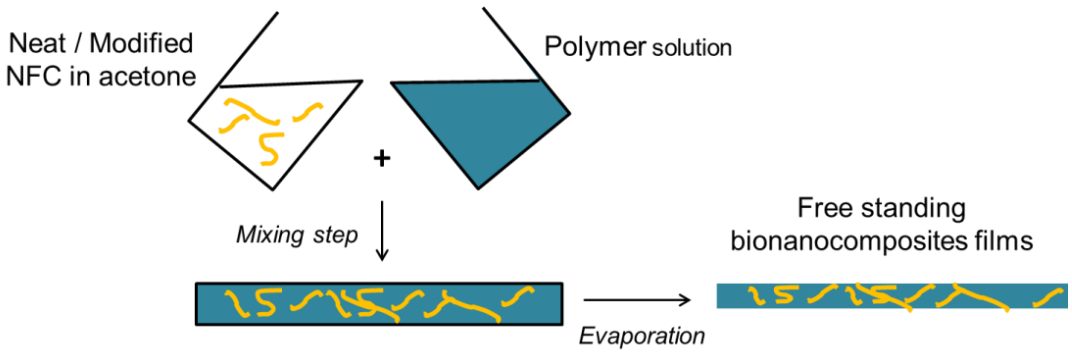

Figure 2-1 : Steps involved in preparation of bionanocomposites

In this first section, the influence of the matrix and notably the compatibility between matrices and the reinforcing elements was checked. For this purpose, neat and modified

NFCs were added to several polymeric matrices and the modified NFC was restricted to NFC_AA, with two loading levels: 2.5 and 10%wt.

Figure 2-2 presents a visual inspection of the obtained bionanocomposite reinforced with neat and NFC_AA. It shows, clearly, that films reinforced with grafted cellulose nanofibrils exhibit a better homogeneity and dispersion of the nanoelements within the matrices, to compare with films reinforced with neat NFC.

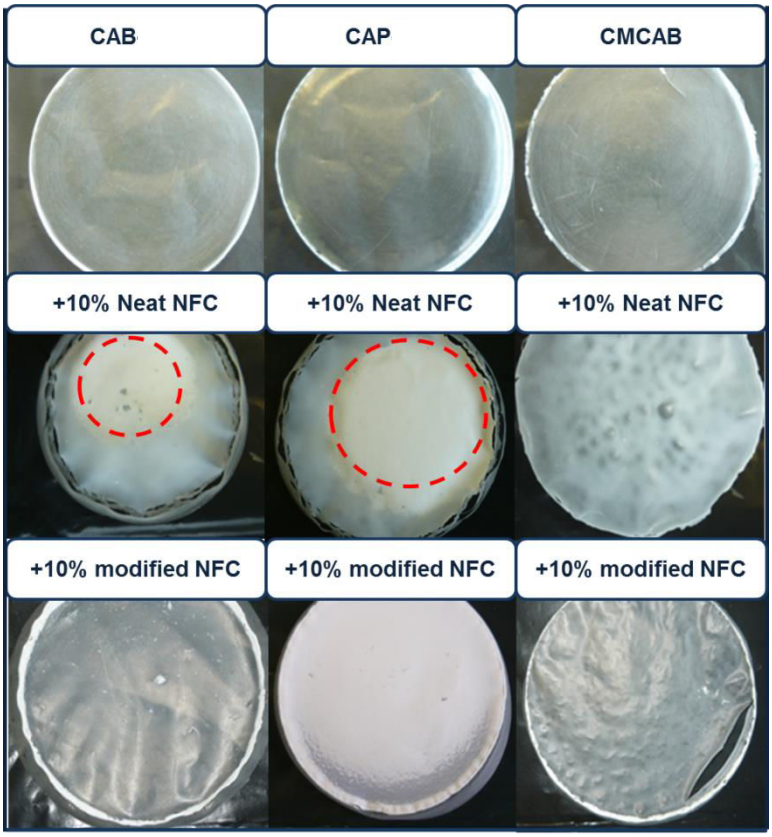

Figure 2-2 : Pictures of films obtained from CAB, CAP and CMCAB reinforced with 10%wt. of neat and modified NFC_AA

Indeed, it has been proven after dissolution and filtration steps (using a sieve with a mesh of 1µm which ensure the retaining of NFC) that the whitish area observed in the center of films reinforced with neat NFC corresponds to a migration of cellulosic nanofillers (dotted circle with higher NFC concentration). Such a migration is probably due to a poor compatibility between the hydrophobic matrix and hydrophilic fillers. Despite a good dispersion of both modified and unmodified cellulosic nanoparticles, CMCAB-based nanocomposite films presented a wrinkled structure. In addition, a visual inspection showed that except for CMCAB-based nanocomposites, the transparence of the films decreased as the amount of filler added increased. Thermal properties investigation by DSC measurements (Dynamic Scattering Calorimetry) was firstly conducted (not shown) in order

to identify the melting temperature of each bionanocomposite. These values are summarized in the Table 2-3.

Table 2-3 : Thermal characteristics obtained for matrices reinforced with 2.5 or 10%wt. of neat or modified NFC

Filler content (wt/wt)		Melting temperature (°C)		
		CAB	**CAP**	**CMCAB**
0%		166	194	155
2.5%	neat NFC	168	198	156
10%	neat NFC	168	197	164
2.5%	modified NFC_AA	168	197	156
10%	modified NFC_AA	168	190	163

The addition of NFC in the polymer matrix reduces the mobility of macromolecular chains thus increasing the melting temperature. Regarding CAB and CAP, no differences are observed whatever the NFC content meaning NFC network is assessed as soon as 2% of NFC is added. On the contrary, melting point clearly increased when quantity of NFC (or NFC_AA) increased with CMCAB. This might be due to a better compatibility with CMCAB (more hydrophilic) allowing polymeric chains flowing at low concentration (i.e. 2%). Higher concentration clearly limits polymer chains flowing by the network of NFC which increased the melting point of the composites.

Similar behavior is observed whatever neat and grafted NFC is concerned, which proves absence of aggregates or defects, except for CAP composites. Indeed CAP-based nanocomposite filled with 10% NFC_AA showed a lower melting temperature compared to that of the neat matrix. This observation results from the poor compatibility between fillers and matrix, which might create defects.

Thanks to DMA technique, thermomechanical properties of bionanocomposites were studied. Figure 2-3 shows the evolution of the normalized storage modulus as a function of the temperature for the three bionanocomposite films. The normalization was performed with the storage modulus value at 40°C.

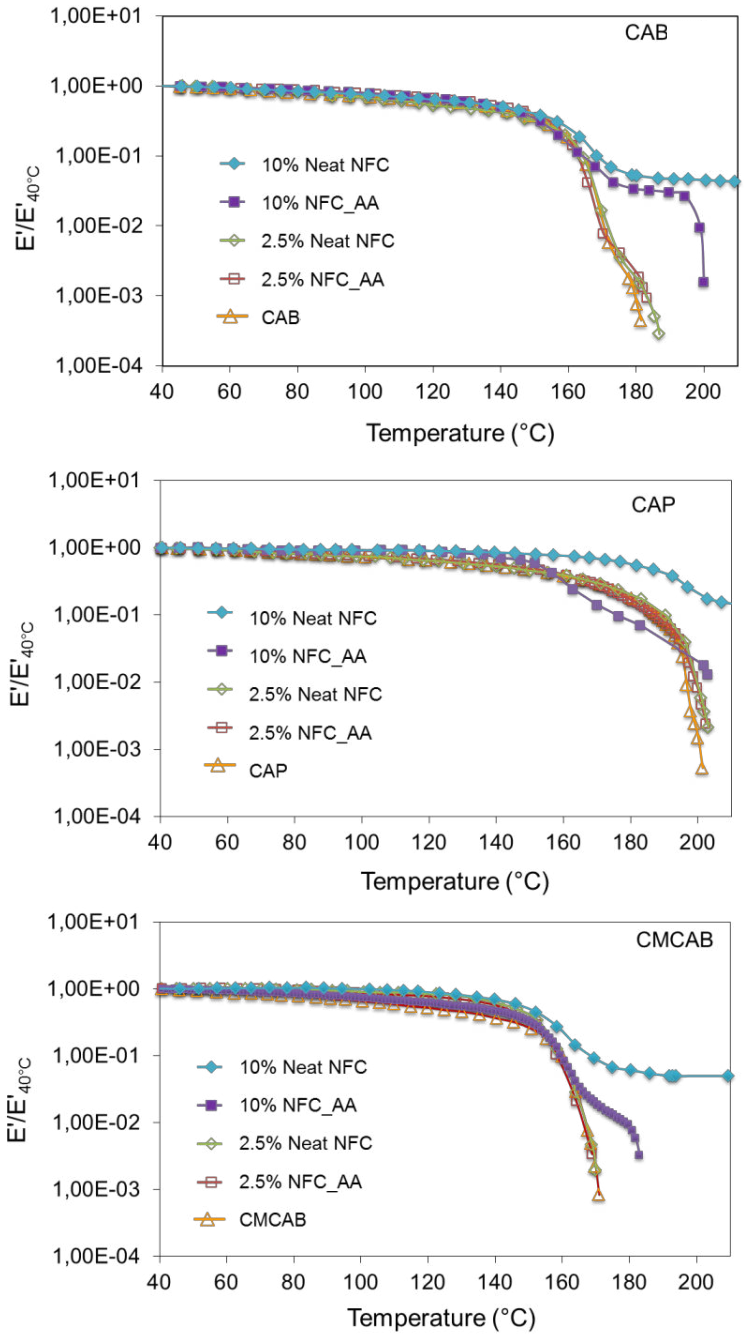

Figure 2-3 : Evolution of the normalized storage modulus, as a function of temperature for CAB, CAP and CMCAB bionanocomposites filled with 2.5% NFC_AA, 2.5 % neat NFC, 10% NFC_AA and 10% neat NFC

The conclusions are similar for all bionanocomposites. Firstly, no significant changes were observed for nanomaterials reinforced with 2.5%wt even with modified NFCs. Indeed, at low filler content, NFCs can form a rigid percolated network within the matrix but not enough to influence thermomechanical behavior of composites. However, for all bionanocomposites reinforced with 10%wt. of neat and modified NFC, a significant improvement of thermomechanical properties was observed. Neat NFC seems to improve thermomechanical properties more than modified NFC. This observation can be probably due to the specific

aggregation and migration of neat NFC in the center of the film discussed before. Consequently, the local concentration of NFC in the choose area is higher than the theoretical value. Another reason can be the fact that, even if the compatibility is better with modified NFC, the network of modified NFC is less stiff than the one of neat NFC due to the lower quantity of hydrogen bonds between grafted NFC.

Furthermore, the addition of cellulosic nanofillers at 10%wt. increases considerably the length of the rubbery plateau, thus allowing the extension of the range of use of the ensuing materials. Siqueira et al. (Siqueira et al. 2011b) who worked on CAB based-nanocomposite materials reinforced with NanoCrystalline Cellulose, have also observed an improvement of the storage modulus with increasing Nanocellulose content (NCC in this case). Similar study reported by Ayuk et al.,(Etang Ayuk et al. 2009) found that CAB-based nanocomposites reinforced with 5%wt. and 10%wt. NCC showed higher storage modulus compared with CAB (i.e., the matrix alone). However, up to our knowledge, the only one study dealing with CAB-NFC nanocomposite did not see such improvement. Indeed Lu et al.,(Lu and Drzal 2010) who worked on cellulose acetate based-nanocomposite reinforced with 5wt% unmodified and APS treated NFC did not find any improvement in the thermo-mechanical properties at high temperature for both kinds of NFC. This might be due to the lower quality of NFC they used, the type of chemical grafting (not adapted) or the matrix selected.

Concerning the other cellulose derivatives (i.e. CAP and CMCAB), reinforcement was less effective. This seems to be mainly due to the much lower quantity of acetyl group (see Table 2-2) displaying a “continuous” interface with NFC_AA. Indeed, no beneficial effect was observed for CAP-based bionanocomposites reinforced with 10%wt. of NFC_AA. On the contrary, a loss of the storage modulus was noticed at a temperature of about 152°C, probably resulting from: (i) the poor compatibility between the matrix and reinforcements and/or (ii) a bad dispersion of NFC within the matrix. CMCAB-based nanocomposites films showed enhanced thermomechanical behavior when filled with both neat and modified NFC. However, the loss of the storage modulus was more pronounced than that of CAB--based bionanocomposites with an extended range of use (prolonged rubbery plateau) of only 14°C.

In conclusion CAB matrix seems to be the best compromise to extend the rubbery plateau of the polymer without a too high decrease of its storage modulus.

In a first conclusion, CAB appears as the most promising matrix for such bionanocomposite applications. For this reason, structural investigation of CAB based bionanocomposites obtained by casting was conducted thanks to FE-SEM analysis.

Micrographs of surface and cross-section of the nanocomposite are presented in Figure 2-4 and Figure 2-5, respectively.

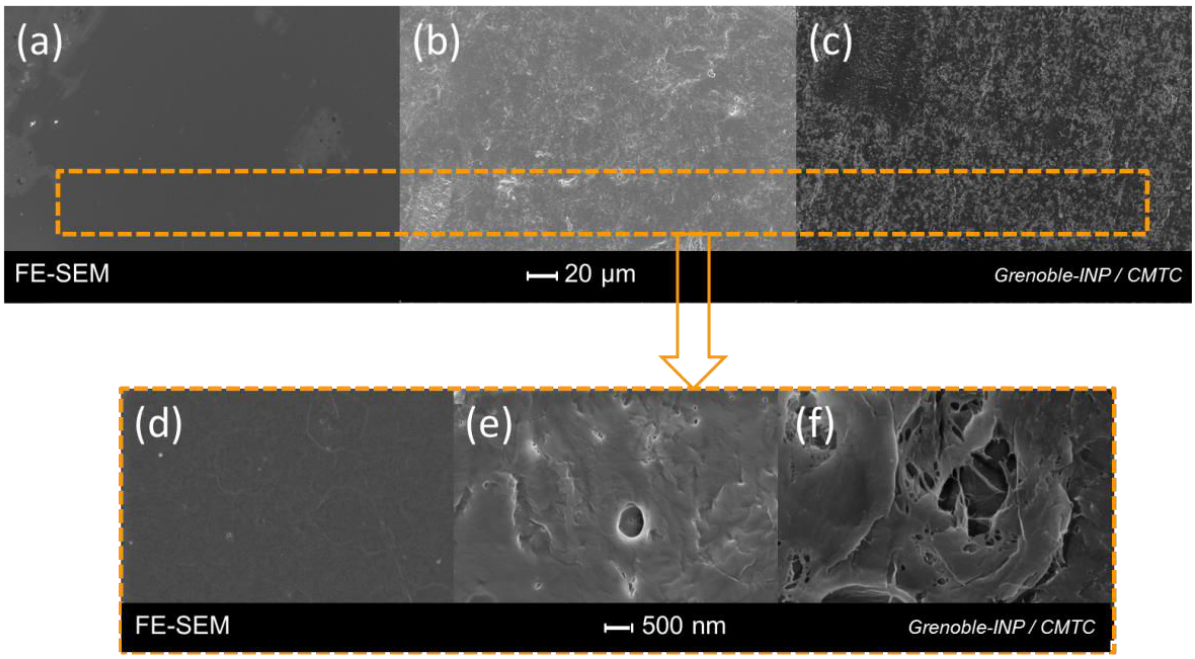

Figure 2-4 : FE-SEM pictures of bionanocomposites at low magnification (a) CAB, (b) CAB filled with 23%wt. of neat NFC, (c) CAB filled with 23% of NFC_AA, whereas pictures (d), (e), and (f) are taken at higher magnification

Cross-section micrographs (Figure 2-5) revealed a good dispersion of both neat and modified NFC in the polymer matrix. However it is difficult to determine whether there is a significant improvement of the dispersion when modified NFCs are used. At a large scale, all composites seem relatively homogeneous but for higher magnifications, significant differences appear (Figure 2-4). Indeed, composite reinforced with NFC_AA exhibit a high porosity at their surface compared to neat matrix. In order to confirm such an argument, water uptake tests were performed on the composites reinforced with neat and modified cellulose nanofibrils.

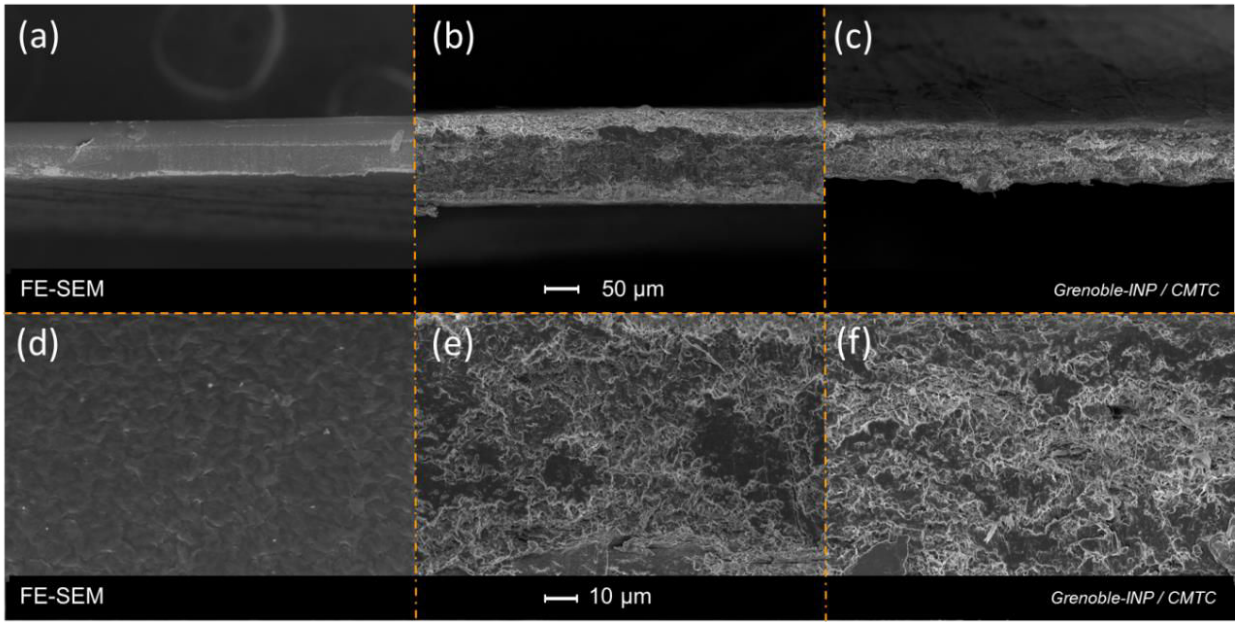

Figure 2-5 : FE-SEM cross section pictures of bionanocomposites at low magnification (a) CAB, (b) CAB filled with 23%wt. of neat NFC, (c) CAB filled with 23% of NFC_AA, whereas pictures (d), (e), and (f) are taken at higher magnification

The data shown in Figure 2-6 confirm the difference in porosity without any doubt. Indeed, the difference of water absorption can be attributed to the difference of porosity. In conclusion, a strong improvement was observed when using both unmodified and modified NFC, with a higher value for modified NFC. With unmodified NFC, it sounds normal as they are hydrophilic and at high percentage some NFC might be at the surface and then available for water absorption. Regarding modified NFC, this can be explained differently by the presence of COO^- group at the surface of modified NFC which will have closer interaction with the solvent used for casting (i.e. the acetone) and then limit its evaporation.

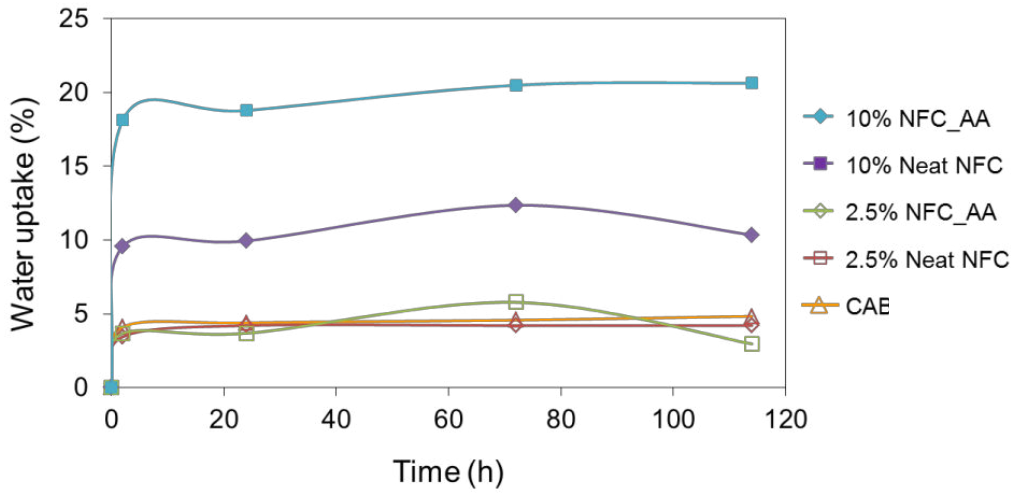

Figure 2-6 : Water Uptake of bionanocomposites reinforced with modified (NFC_AA) and neat NFC

In spite of this porosity, no clear difference in dispersion are visible and we should keep in mind that with the addition of 10%wt. of NFC_AA, it is possible to obtain a well dispersed film having an increased range of use by up to 30°C. For this reason, the next part of this study will focus on CAB as a matrix and will test different type of grafting with an increase of hydrophobic behavior.

2.3.3 Influence of chemical grafting length

Thus, the influence of the length of the grafted aliphatic chain (i.e. NFC_AA, NFC_BA and NFC_HA) as well as the use of several nanofiber loadings (i.e. 10%wt. and 23%wt.) on the resulting nanocomposites has been investigated.

First of all, in this section, the influence of grafting on the thermal degradation of CAB nanocomposites has been studied. Only one kind of bionanocomposites is discussed in details, but the conclusion concerning the rest of the samples (data not shown) will be drawn. As presented in the Figure 2-7, CAB-based nanocomposite films reinforced with 10% of both neat and modified NFC (NFC_HA) show an initial weight loss (2-3%wt.) at about 60-100°C, which results from the loss of moisture upon heating.

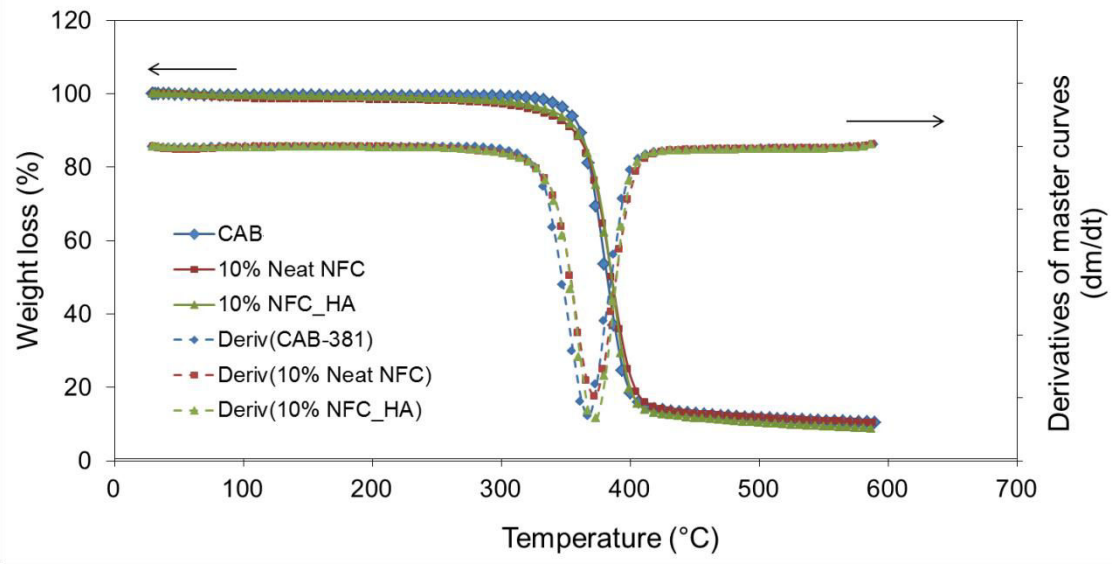

Figure 2-7 : Thermogravimetric analyses curves and their derivatives of CAB and its bionanocomposites filled with 10% of neat NFC and NFC_HA

CAB matrix is thermally stable and exhibits a major degradation peak at 370°C. The decomposition of cellulose is basically a result of inter- or intra-molecular dehydration reaction. Thus cellulose acetates derivatives have a better thermal stability due to the small number of remaining free hydroxyl groups left after chemical modification. Indeed, carbon NMR (see Table 2-2) analysis performed on CAB revealed that the degree of substitution for

hydroxyl groups was found to be about 2.7, whereas elemental analysis (EA) carried out on modified NFC indicated a degree of substitution of 0.3. In conclusion, the addition of NFC (modified or not) in the polymer matrix does not affect the thermal stability of the polymer in spite of this difference of chemistry. Similar results were found by Lu et al.,(Lu and Drzal 2010) for CA-based nanocomposite reinforced with unmodified and APS treated NFC. These results are promising for the rest of the study, because the good thermal stability presented by the matrix is not negatively affected by the addition of thermally less stable cellulosic nanofibers. Indeed, bionanocomposites start to degrade at a temperature of about 315-320°C depending on the filler loadings, whereas for neat matrix the degradation starts to occur at a temperature of 330-335°C.

Consequently, thermomechanical properties of CAB--based bionanocomposites can be assessed and are presented in Figure 2-8. All obtained data are normalized with the storage modulus obtained at 40°C.

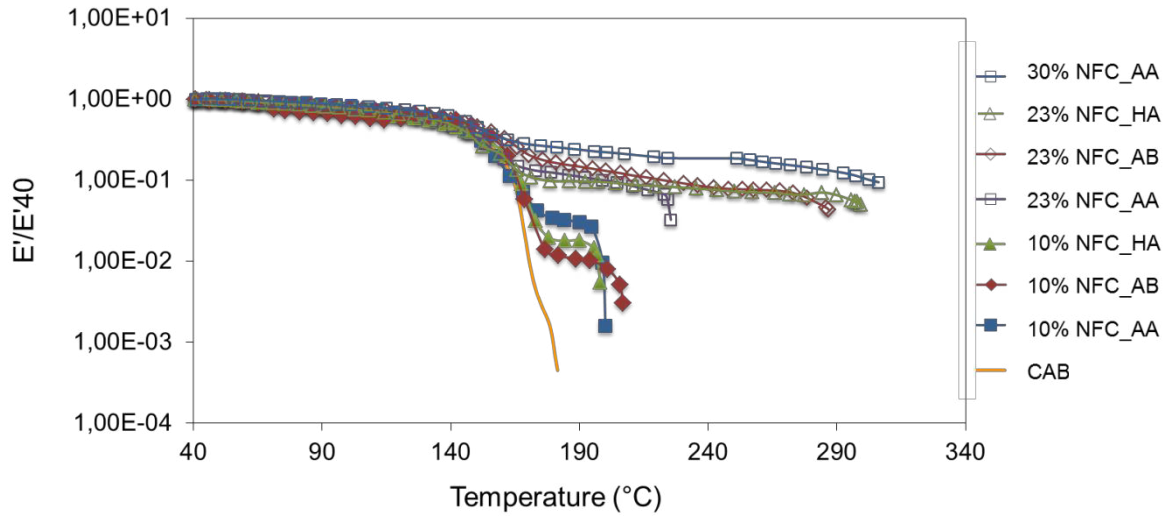

Figure 2-8 : Evolution of the normalized storage modulus as a function of temperature for CAB-based bionanocomposites films reinforced with NFC_AA, NFC_AB and NFC_HA, respectively

This figure shows very promising results. In fact, compared to the neat matrix, the storage modulus of CAB--based bionanocomposites remains relatively high for temperatures higher than the flow temperature of CAB at about 170°C. Indeed, higher is the amount of added cellulosic nanofillers, softer is the loss of the storage modulus at 170°C. Thus, the storage modulus at 180°C of reinforced bionanocomposites is divided by 100 (compared to storage modulus at 40°C) for nanocomposites loaded with 10%wt. of NFC and only by 10 when 23%wt. of NFC is added. The storage modulus of neat matrix cannot even be measured at 180°C, proving clearly the positive impact. Indeed, CAB alone cannot be used beyond 170°C

whereas CAB-based bionanocomposites are still usable up to 250-280°C. Such a significant improvement has never been mentioned in the literature regarding CAB-based bionanocomposites reinforced with cellulosic nanofiller (neither NFC nor NCC). However, it is difficult to conclude on the influence of grafting moieties type on the thermomechanical properties of the obtained nanomaterials. It seems that higher is the length of the aliphatic chain lower is the reinforcing effect. That is why Figure 2-9 shows the comparison of the evolution of storage modulus, as a function of temperature for CAB-based bionanocomposites reinforced with two kinds of modified fillers neat NFC and NFC_HA for both loading levels.

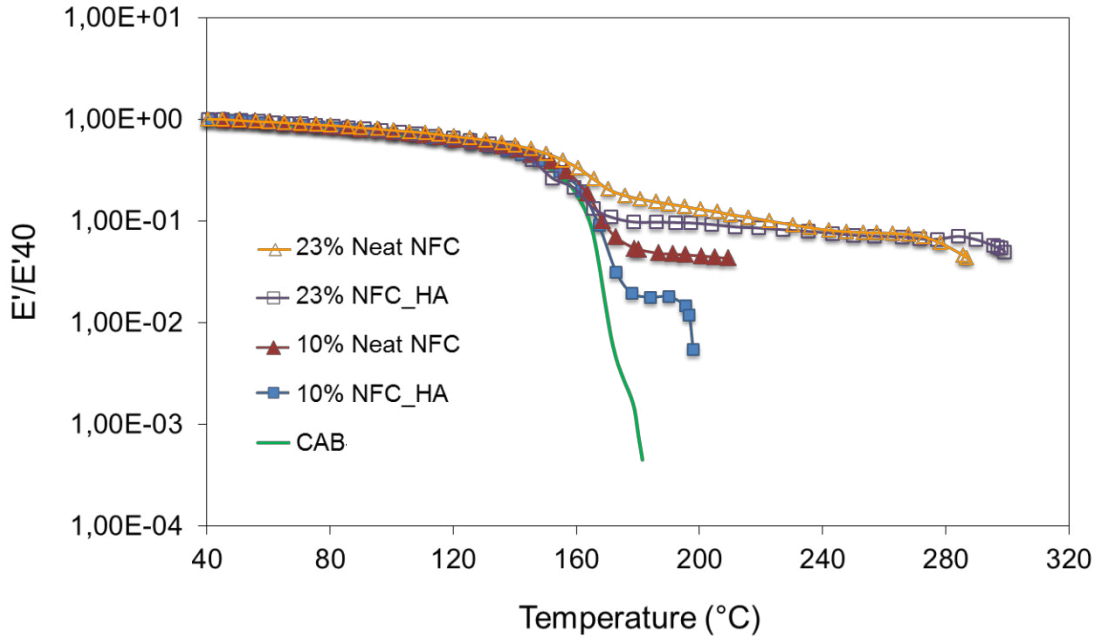

Figure 2-9 : Evolution of the normalized storage modulus as a function of temperature for CAB-based nanocomposites films reinforced with neat NFC or NFC_HA at 10% and 23%wt

As shown in Figure 2-9, films reinforced with neat NFC exhibit better thermomechanical properties than nanomaterials reinforced with modified counterpart. Indeed, thermomechanical strength of nanocomposite is given by the (i) dispersion ability and (ii) the compatibility with the matrix but also by (iii) the ability of nanofillers to form within the material a rigid percolated network. Within this compromise, the chemical modification of nanofibrillated cellulose should improve dispersion and compatibility but also limits strongly hydrogen bond interactions, thus weakening the nanofibrous network. The contact angle measurement (Table 2-1) clearly shows the difference between NFC_HA and NFC_AA, and obviously neat NFC. If we evaporate the suspension of grafted NFC alone, a clear film is obtained with neat NFC, a non-homogeneous network (but a network) film can be formed with suspension of NFC_AA, but for other grafting, a powder is obtained indicating that the

chemical treatment induced weaker interactions between the nanofibers (hydrogen bonds breakage). Neat NFC, instead, can form a rigid network within the matrix, thus forming the backbone of the material. Obviously, better is the network structure, higher are the thermomechanical properties, as reported by Lu et al. (Lu and Drzal 2010) who explained the same feature by the capacity of NFC to form a strong network thanks to hydrogen interactions. To conclude on the effect of the grafting, it could be said that the improvement in thermomechanical properties is not only governed by any improvement in the wettability between fillers and matrix but rather influences by the ability for fillers to form a structured network giving the required stiffness to the material under investigation.

2.4 Conclusions

Composites entirely made from renewable, bio-based sources were successfully prepared using NFC, as the reinforcing phase and cellulose ester as matrices. As expected the use of cellulose nanofibrils as filler reinforcements in cellulose acetate matrices improves significantly the thermomechanical properties of bionanocomposites obtained by a casting/evaporation technique. Indeed, the addition of 10%wt. of neat or modified NFC extended the length of the rubbery plateau by 10 to 30°C, depending on both the used filler and the matrix. The most interesting reinforcement was observed using CAB as matrix.

Films filled with grafted cellulose nanofibrils exhibited better homogeneity than those reinforced with neat NFC. Indeed, an aggregation phenomenon of neat NFC was observed within bionanocomposite films reinforced with 10%wt. of neat NFC.

Furthermore, it is difficult to conclude on the influence of grafting on the reinforcing properties of cellulosic nanofillers. It seems that higher is the length of the aliphatic chain, lower is the reinforcing effect. The dispersion is certainly improved in the case of grafted cellulose nanofibrils due to their hydrophobic nature, but the most important thing considering the thermomechanical properties is the ability of NFC to build a rigid network within the matrix. Generally speaking, the more the network is structured, the more the thermomechanical properties are improved.

Acknowledgment

This research was supported by the "Scale-Up of Nanoparticles in modern PAPermaking" (SUNPAP) project of the seven framework program of European research under grant agreement n°228802. Authors want to thank Alain Dufresne and Cécile Bruzzese-Sillard for their help in comprehension of results and DMA measurements.

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3. Antimicrobial activity and biodegradability assessment of chemically grafted nanofibrillated cellulose

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Abstract

Nanofibrillated cellulose (NFC) and their derivatives were prepared using three chemical surface modifications strategies. All grafting were characterized by FTIR and contact angle measurements in order to evaluate the efficiency of grafting. Antibacterial activities of neat and grafted samples were investigated against two kinds of bacteria (i.e. Gram + (Staphylococcus aureus) and Gram - (Klebsiella pneumoniae)). All the grafted samples displayed promising results with at least bacteriostatic effect or bactericidal properties. They also strongly enhanced the photo-catalytic antimicrobial effect of TiO2. This study proves that it is better to use grafted NFC either alone or for functionalization with TiO2 if anti-bacterial properties are desired. The cellulose backbone is known to be easily biodegradable in different biodegradation conditions and environments. The chemical surface modifications applied on NFC in the present work did not negatively influence this valuable property of cellulose but help for monitoring this property, which could be very useful for paper, packaging and composites.

Keywords

Nanofibrillated cellulose; Surface grafting; Biodegradability; Antimicrobial properties

***Inspired from**: Karim Missoum, Patrizia Sadocco, Naceur Belgacem, Julien Bras – Reactive and Functional Polymers (2013) – Accepted*

3.1 Introduction

Due to the renewable nature, abundance, biocompatibility, biodegradability and high specific strength of cellulose fibers, a growing interest has been devoted to the ensued NanoFibrillated Cellulose (NFC). NFCs were produced and isolated first in 1983 by Tubark et al. (Turbak et al. 1983) using high pressure homogenizer process. Presently, nanofibrillated cellulose can be obtained, from cellulose fibers by different mechanical and/or chemical pretreatment methods (Henriksson et al. 2007; Isogai et al. 2011; Pääkkö et al. 2007; Siró and Plackett 2010b), in the form of long flexible filament in aqueous suspensions displaying a range in diameter of 5 to 50 nm diameter and several micrometers in length. Their specific surface areas combined with remarkable strength and flexibility make them a good candidate in different applications. Very recent reviews are available in the literature dealing with their properties and their potential applications in composite, paper and packaging for example (Eichhorn et al. 2010; Isogai et al. 2011; Klemm et al. 2009; Lavoine et al. 2012; Moon et al. 2011).

However, these advantages turn to constitute their drawbacks. The high viscosity at very low concentration (i.e. 2-5%wt.) and their ability to form films or aggregates once dried limit their use in some applications. Chemical surface modification (Filpponen et al. 2012; Missoum et al. 2012a; Pahimanolis et al. 2011; Rodionova et al. 2011; Syverud et al. 2011) on hydroxyl groups of NFC has been developed last decade by scientists to overcome these limitations. However such treatments can be costly and only added value applications should be envisaged with such materials. Therefore, it could be interesting to add new functions like antimicrobial as already performed on chitosan substrates (Belalia et al. 2008; Bordenave et al. 2010).

NFC has been explored for numerous innovative applications, including composites, emulsions and also viscosity modifier. However, NFC based materials for antimicrobial activity has not yet been fully explored. Only very few scientific papers (only 5 papers up to our knowledge) exists (Andresen et al. 2007; Díez et al. 2011; Martins et al. 2012; Sadocco et al. 2012; Syverud et al. 2011) and usually in this scientific papers, silver nanoparticles have been tested after adsorption onto NFC (contrary to our chemical grafting strategy). However, the release of inorganic nanoparticles might be an issue when health and safety is concerned and the future availability of these non-renewable materials might be an issue for the development of this solution. In addition a growing interest in antimicrobial development brought by metal oxide nanoparticles like MgO, ZnO or TiO_2 particles has been recently published (Huang et al. 2005; Jones et al. 2008; Marciano et al. 2009). In this case, the development of bacterial resistance is less favored because these nanomaterials attack a

broad range of bacteria. Among them, TiO_2 nanoparticles have attracted particular interest and were successfully applied with cellulosic fibers (Daoud et al. 2005; Vasilev et al. 2009; Visai et al. 2011). The first results about NFC-TiO_2 have been presented this year (Sadocco et al. 2012). Based on photo-catalytic activation, TiO_2 nanoparticles have lethal effects on the cells; they can damage DNA, cell membranes, cell proteins and may lead to cell death.

In spite of these studies, almost nobody (to our knowledge) tested the chemically modified NFC in this context. Indeed, even if some surfactant adsorption has already been tested for anti-microbial properties (Syverud et al. 2011), only one paper (Andresen et al. 2007) deals with chemical grafting of quaternary ammonium molecule via silane reaction.

No other grafted chemical functions have been tested whereas are well-known to have bactericidal (like carbamates, for instance) (Ray et al. 2005). That is why this study deals with the effect of different chemical modification of NFC on the anti-bacterial properties with a view to using these “active” particles directly at the surface or into the materials bulk for paper, packaging or composites applications. In such a case NFC should be active but also should keep (or help to control) their biodegradable character.

Indeed, cellulose is a well-known biodegradable polymer, in fact pure cellulose is usually recommended as the positive reference in the biodegradation tests (Frisoni et al. 2001). However, in some applications like external application (e.g. Mulch), a lower kinetic of biodegradability is expected. Moreover, it has been recently shown that addition of nano-cellulose in composite can increase their degradation kinetics (Hassan et al. 2012). It is not always the expectation in nano-composite. So this information is a key property for monitoring material end-of-life. To the best of our knowledge, biodegradability of modified NFC was never reported in literature.

The research described in this study involved neat and grafted NFC (by carbanilation and esterification) in order to check their anti-bacterial and biodegradation properties. The antibacterial activity has been evaluated against Gram positive (*Staphylococcus aureus*) and Gram negative (*Klebsiella pneumoniae*) bacteria and the mechanism of antibacterial action has been discussed. Moreover, neat and grafted NFCs were functionalized or not with TiO_2 nanoparticles to enhance their antibacterial properties and to check the influence of chemical grafting. To the best of our knowledge, this is the first time that a paper dealing with both bactericidal effect and biodegradation behavior of neat and chemically modified NFC is reported.

3.2 Experimental

3.2.1 Materials

The wood pulp was kindly delivered by Domsjö (Sweden) and corresponded to a mix between Spruce and Pine (60% and 40%, respectively). This material is a dissolving pulp referred to sodium based sulfite mill extraction and used for the production of NFC. A second wood pulp was used in this study for the chemical modification using Eucalyptus as raw material for the production of NFC. Endoglucanase used for the pretreatment of cellulosic fibers was purchased in Novozyme (Denmark).

The coupling agent (n-octadecyl isocyanate - 98%) and the catalyst (dibutyltin dilaurate - 96%), as well as the other reagents, acetic (99%), butyric (99%), iso-butyric (99%) and hexanoic anhydrides (99%), the ionic liquid [bmim][PF6] (98% HPLC grade), all the solvents used (i.e. ethanol-98%, acetone-98%, toluene-98% and dichloromethane-98%) and the surfactant TetradecylTrimethylAmmonium Bromide (TTAB), with a purity of 99%, were purchased from Sigma-Aldrich (FRANCE). AlkylKetene Dimer (AKD) was kindly supplied by Hercules©. It corresponds to a pure liquid AKD without stabilizer (Prequel 9000). Distilled water was used for all experiments.

Titanium dioxide nanoparticles were supplied by Colorobbia (Italy) and dispersions were synthesized via hydrolysis and condensation of alkoxide-based precursors in water.

All microbial strains used were provided by DSMZ, Deutsche Sammlung von Mikroorganismen und Zellkulturen GmbH (German Collection of Microorganisms and Cell Cultures). *Staphylococcus aureus* ATCC 6538 (DSM 799) and *Klebsiella pneumoniae* ATCC 4352 (DSM 789) were maintained frozen (-80 °C) and transferred monthly on PCA (Plate Count Agar) made of 5 g/L tryptone; 2.5 g/L yeast extract; 1 g/L glucose and 9 g/L neutralized bacteriological agar.

3.2.2 Neat and modified NFC preparation

Nanofibrillated cellulose suspension was produced from wood pulp depending on the chemical grafting strategy. Eucalyptus was used for carbanilated NFC and Domsjö pulp for all the other treatments and neat NFC. Authors asses the hypothesis that pulp source has no influence for this study. A suspension of bleached cellulose fibers (2.0%wt.) was enzymatically pretreated with endoglucanase (Cellulase) during 1h at 50°C to facilitate the size reduction of the fibers. Then, the slurry was fibrillated using a Masuko Grinder© (Japan). Size reduction of the fibers into nanofibrillated cellulose was obtained after 10 passes

between the rotating and the static stones at 1,500 rpm. Solid content of the NFC suspension was around 2.6% (w/w).

Six grades of modified NFC (3g of each) were produced following previously described procedures. The first grade (NFC_C_{18}NCO) is obtained by carbanilation of NFC in toluene (Missoum et al. 2012c). The three next samples obtained with acetic, butyric, hexanoic anhydrides, i.e. NFC_AA, NFC_BA, NFC_HA, respectively, were produced following a procedure in ionic liquid detailed very recently (Missoum et al. 2012a). The last surface chemical modification of NFC was performed using a nanoemulsion of Alkyl Ketone Dimer (NFC_AKD) (Missoum et al. 2012b).

The adsorption of titanium dioxide was performed with the 30 ml NFC (600mg dry NFC) + "x" ml TiO_2 to obtain different NFC:TiO_2 ratios. After mixing, centrifugation steps (3 times, 15 min at 10.000 rpm) with water were done to eliminate excess TiO_2 not "adsorbed" to NFC. Final residue was suspended in about 6-7 ml of water giving suspensions at 5-7% dry weight. The reference sample with NFC followed similar treatment: 30 ml NFC (600mg dry NFC) + centrifugation (3 times, 15 min at 10.000 rpm) with water. A control test was performed to evaluate the amount of TiO2 retained by NFC: in fact some control preparations were obtained by filtration procedures. Instead of centrifugation, the NFC/TiO_2 suspension was filtered on glass fiber filters, to eliminate excess TiO_2 not attached to NFC (10 ml suspension was washed with 30 ml of water). The final NFC/TiO_2 nanocomposite was tested for antibacterial properties and similar activities were obtained in respect to the preparations obtained by centrifugation.

3.2.3 NFC characterizations

Microscopy characterization were carried out using a scanning electron microscope equipped with a field emission gun (FE-SEM), model Zeiss Ultra column 55 Gemini, was used to observe neat and modified NFC. The accelerating voltage (EHT) was 3kV for a working distance of 6.4 mm. The sample tested was deposited onto a substrate covered with carbon tape and then coated with a 2 nm layer of Au/Pd (Gold/Palladium) to ensure the conductivity of samples. The coating was obtained by sputtering Au/Pd atoms under a voltage of 6kV and 300µA during 20s.

Infrared spectra were recorded on film for neat NFC and dried powder for modified NFC, using a Perkin-Elmer SP100 spectrometer. For each sample, the Diamond crystal of an attenuate total reflectance (ATR) apparatus was used. The torque applied was kept constant to ensure a same pressure on each sample. Triplicates were performed for each samples

and best representative spectrum were kept for consideration. All spectra were recorded between 4000 and 600 cm^{-1}, with a resolution of 4 cm^{-1} and 8 scans.

Contact angle measurements were carried out by depositing different water droplets at the surface of the studied substrates and by recording the formed angles using an OCA dataphysics system equipped with a CCD camera. The contact angle and the drop volume (5µl) acquisition were realized during the first after deposition seconds until equilibrium has been achieved and taking 4images/s. For unmodified NFC and modified NFC, the measurement was performed on dried films. All measurements were performed at least 5 times for each sample and averaged.

3.2.4 Assessment of antibacterial activity of neat and modified NFC

The microorganisms, i.e. *S.aureus*, *K. pneumoniae* were tested on neat and grafted NFC. 4mg dry (weights of NFC (from a suspension at 2.6%wt.) were tested for each sample. The samples, dispersed in acetone after chemical grafting procedure (see previous paper), were washed by centrifugation at 15000 rpm, 18°C, for 20 minutes. The supernatant was eliminated and the samples were washed 4 times with 20 mL of water at 15000 rpm, 18°C for 20 minutes.

In the presence of light, the inoculated samples by *S.aureus* and K.pneumoniae were pre-exposed to standard solar lamp (8000 Lux) for 4h at room temperature this exposure is necessary for the activation of photo-catalytic behavior of TiO_2 nanoparticles, the samples were then incubated in the dark for 20h at 37°C. At the end of the incubation period the bacteria were extracted from the samples under investigation by using a neutralizing solution. The number of living cells (CFU = colony forming units) in the extracted suspension was evaluated by count plate agar method. Specifically the following testing conditions were adopted for testing microorganisms: Gram positive bacteria: *S.aureus* ATCC 6538 and Gram negative: *K. pneumoniae* ATCC 4352. 100 µL of a solution of 12.5% diluted NB in physiological saline with an initial number of bacteria of about 1x106 CFU/ml was used as inoculum.

At the end of antibacterial tests the surviving bacteria were extracted by using 50 ml of neutralizing solution: Azolectin 3 g/L, Polysorbate 80 30 g/L, sodium thiosulphate 5 g/L, L-Hystidine 1 g/L, KH2PO4 0.68 g/L, (pH a 7.2 ± 0.2). The nanocellulose was washed by neutralising solution and filtered. The absence of retention of bacteria on NFC was checked

with the reference samples at contact time zero. The number of extracted bacteria corresponded to what inoculated.

The samples were subjected to sterilization using an autoclave. The antibacterial activity of the sample, as bacteria log reduction, was calculated as follows:

$$\log reduction = logCFU\ T_{24}\ \text{blank (control)} - \ logCFU\ T_{24}\ \text{sample}$$

Where: CFU T_{24} is the colony forming number corresponding to the bacteria living cells at time 24 h. The tested concentration of bacteria is related to what applied in standard methods for finished products. They are quite common for textiles as well as plastics test methods.

3.2.5 Biodegradability of Neat and grafted NFC

The test was conducted according to the standard method ISO 14852:1999. The complete transformation (mineralization) of the organic carbon contained in the sample to CO_2 and water by the action of the microorganisms was measured. The ultimate biodegradation test was conducted by dispersing the sample in an aqueous medium.

The used reactors are 5L glass vessels corresponding to 2 blank sample-free reactors, 2 reactors with neat NFC as reference, 2 reactors for each grafted sample and 1 reactor with sodium benzoate as biodegradable positive reference. The aqueous media used is composed of 3L of saline/buffer solution as described in the standard method.

The inoculum for each reactor was 30mL water extract obtained by soil and mature compost. Samples tested were film for neat NFC and dried powder for modified NFC. About 200 mg of each sample for each reactor (corresponding to around 100 mg of organic carbon content) were introduced in each reactor, equipped with inlet and outlet tubes for the aeration with compressed humidified air. The CO_2 was previously removed from the inlet air by adsorption on soda lime. The test was conducted at 25 ± 2°C.

The CO_2 produced from each reactor was adsorbed in barium hydroxide solution $Ba(OH)_2$, which reacts with CO_2 and therefore, barium carbonate is precipitated. The amount of CO_2 evolved is determined by titration of the remaining $Ba(OH)_2$ with hydrochloric acid (HCl).

The percentage of biodegradation was expressed as % of CO_2 production with respect to the theoretical CO_2 content of the sample (%Theor.CO_2).

The tests were conducted in duplicate and then averaged.

3.3 Results and discussions

3.3.1 NFCs characterizations

Neat and modified NFCs (i.e. NFC_C18NCO, NFC_AA, NFC_BA, NFC_HA and NFC_AKD) were first characterized with the FE-SEM technique, as presented in Figure 3-1.

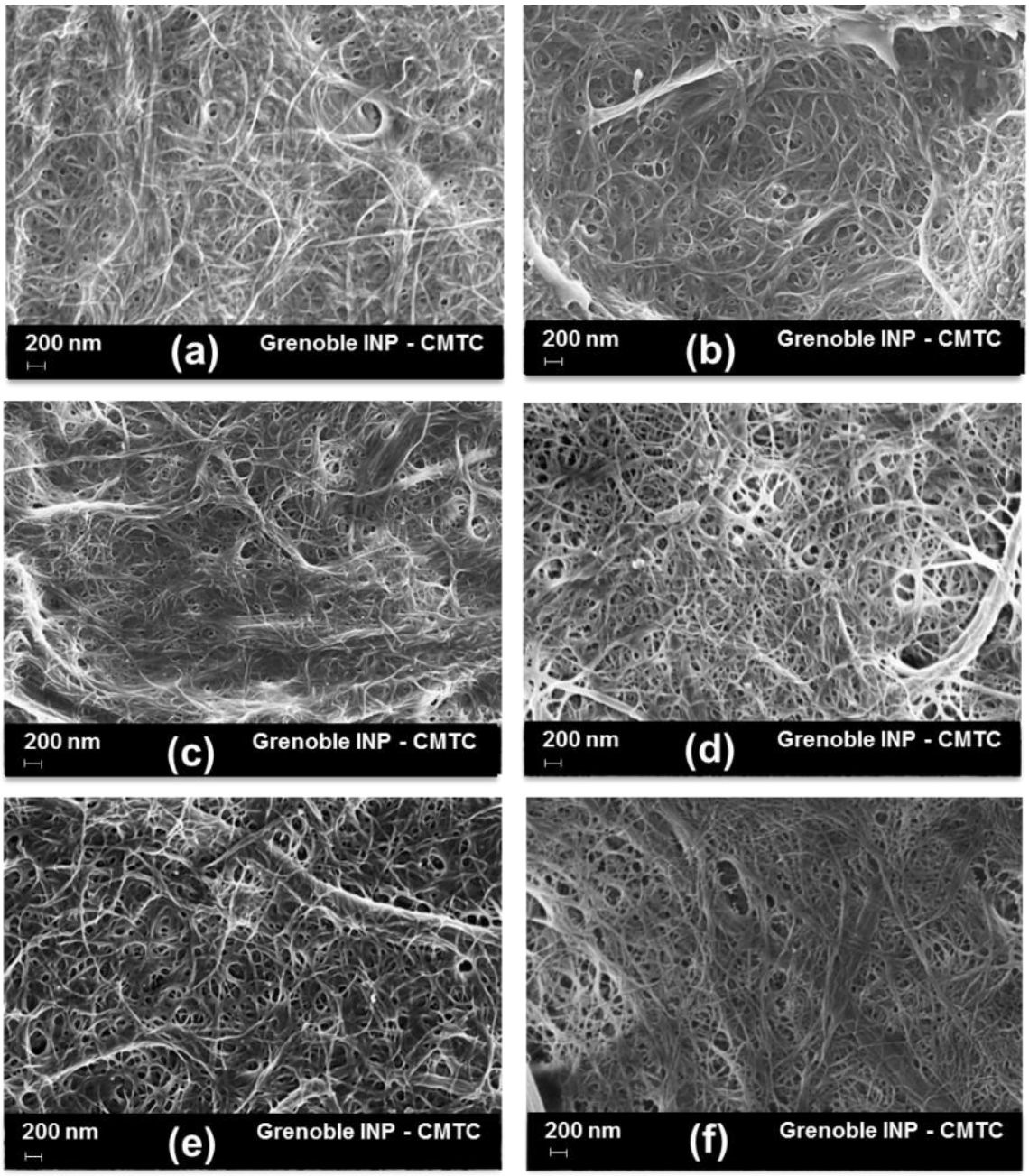

Figure 3-1 : FE-SEM pictures of (a) neat NFC and modified NFC with (b) octadecyl isocyanate, (c) acetic anhydride, (d) butyric anhydride, (e) hexanoic anhydride and (f) alkyl ketone dimer nanoemulsion

The diameter of the nanofibrillated cellulose was determined by digital image analysis (ImageJ) of FE-SEM pictures. The average diameter of neat NFC was about 22 ± 5nm (a minimum of 50 measurements was performed with at least 3 independent images). The micrograph (Figure 3-1/a) shows that nanofibrils are strongly entangled. After grafting, FE-SEM micrographs of NFC show similar average diameter 34 ± 9nm, 36 ± 12nm, 40± 16nm, 54 ± 15nm and 31 ± 8 nm for NFC_C18NCO, NFC_AA, NFC_BA, NFC_HA and NFC_AKD respectively. In all case the fibrillar structure is conserved and a slight increase in diameter is observed. It is worth to note that no morphology modifications are observed after grafting but NFC seems to be less entangled, most probably because of lower hydrogen bonds between NFC elements even if SEM sample preparation can also influence this entanglement.

FTIR spectroscopy was used to control the grafting for the different reaction conditions. Figure 3-2 shows FTIR spectra of the samples after extensive washing. Before treatment, the cellulosic nano-fibers display several bands characteristic to cellulose macromolecules at 3350cm^{-1} (ν_{OH}), 1110cm^{-1} (ν_{C-O}) (used for the normalization of all spectra) and 2868 and 2970cm^{-1} (ν_{CHx})..

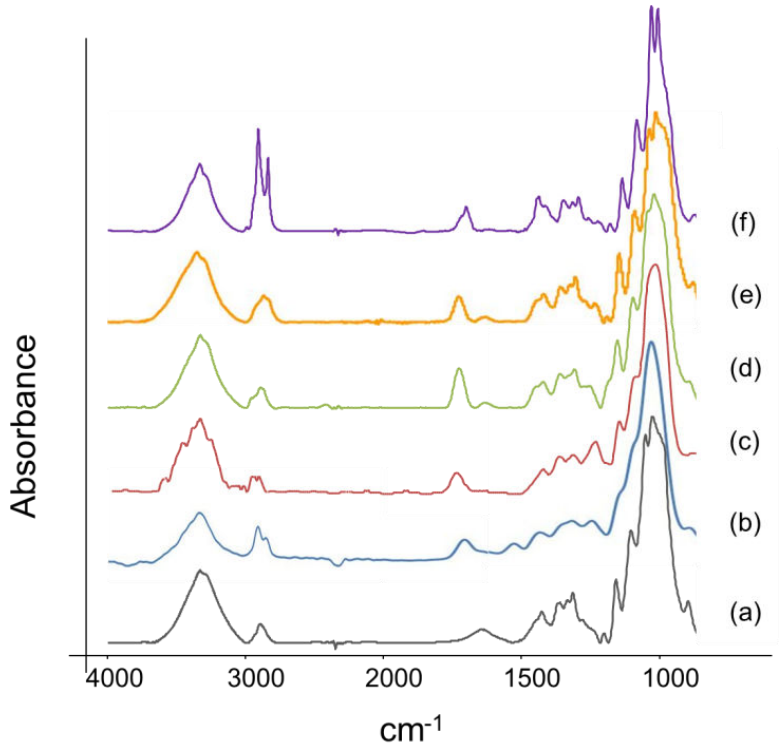

Figure 3-2 : Fourier Transformation Infra-Red spectra obtained for (a) neat NFC and modified NFC with (b) octadecyl isocyanate, (c) acetic anhydride, (d) butyric anhydride, (e) hexanoic anhydride and (f) alkyl ketone dimer nanoemulsion

After carbanilation or esterification reactions, a characteristic peak assigned to carbamate and ester bonds at 1735cm^{-1} and 1750cm^{-1} respectively (Fig.2b-2f), has clearly appeared. An increase of the bands at 2868 and 2970cm^{-1} corresponding to asymmetric and symmetric – CH_2 – stretches from aliphatic chain was also observed. These observations allow saying that NFCs are chemically modified because all of NFC grafted have been extensively washed by Soxhlet extraction before any use and analysis. Moreover chemical grafting characterization are deeply precise with performing analytic tool (e.g. XPS, TOF-SIMS) in our previous work (Missoum et al. 2012a), in which clear covalent grafting have been assessed with a degree of substitution between 0.1 and 0.3.

Contact angle measurements were also performed in order to point out the hydrophobic behavior of the grafted nanofibers comparing to neat counterpart. The results are presented in the Table 3-1. As expected the contact angle values of a drop of water deposited on the surface of the grafted NFC are higher than those found for the neat NFC.

Table 3-1 : Contact angle value obtained with water for Neat NFC and modified NFC

Samples	**Contact angle values**
Neat NFC	20°
NFC_C_{18}NCO	79.5° +/- 1°
NFC_AA	56° +/- 1°
NFC_BA	98.6° +/- 1°
NFC_HA	104.8° +/- 0.7°
NFC_AKD	120° +/- 2°

The neat NFC displayed a decrease of the contact angle value with the time and vanished at 20°. The values of the grafted samples are stable during the acquisition and they are higher than those found for neat NFC surface, namely: 80°, 56°, 99°, 105° and 120° for octadecyl isocyanate acetic, butyric, hexanoic anhydride and AKD grafting, respectively. Water contact angle also confirms, although indirectly, the surface modification.

3.3.2 Antibacterial activity of grafted NFC

The antibacterial activity of modified suspensions was tested towards gram positive (*S.aureus*) and gram negative (*K. Pneumoniae*) bacteria. All the tests were performed in the presence of nutrients (12.5 % diluted nutrient broth) in the buffer testing media (bacteria growing conditions). In these conditions, the antimicrobial activity can be evaluated either as

(i) bactericidal effect: reduction (killing) of the number of bacteria initially inoculated (at least 1 log reduction with respect to the inoculated bacteria, CFU at time 0), or as (ii) bacteriostatic effect: inhibition of bacteria growth, at least 1 log reduction respect to growth in the control sample at time 24h.

Antibacterial tests carried out on modified NFC revealed distinct behavior depending on the applied grafting.

First, Gram positive bacteria were tested, as shown in Figure 3-3, from which it can be seen that neat NFC causes a slight growth regarding *S.aureus* comparing to the control samples represented by the line at 5.5. On the contrary, NFC_C_{18}NCO sample causes a weak reduction on bacterial growth. Their possible mode of action involves bacterial protein denaturation, damage of lipid complexes in cell membranes or dehydration of bacterial cells. Carbamate functions have already been studied for their antimicrobial properties and can display an effective antimicrobial activity. Concerning grafted NFC with anhydrides (see Figure 3-3), no inhibition is assessed with NFC_AA and NFC_BA comparing to neat NFC.

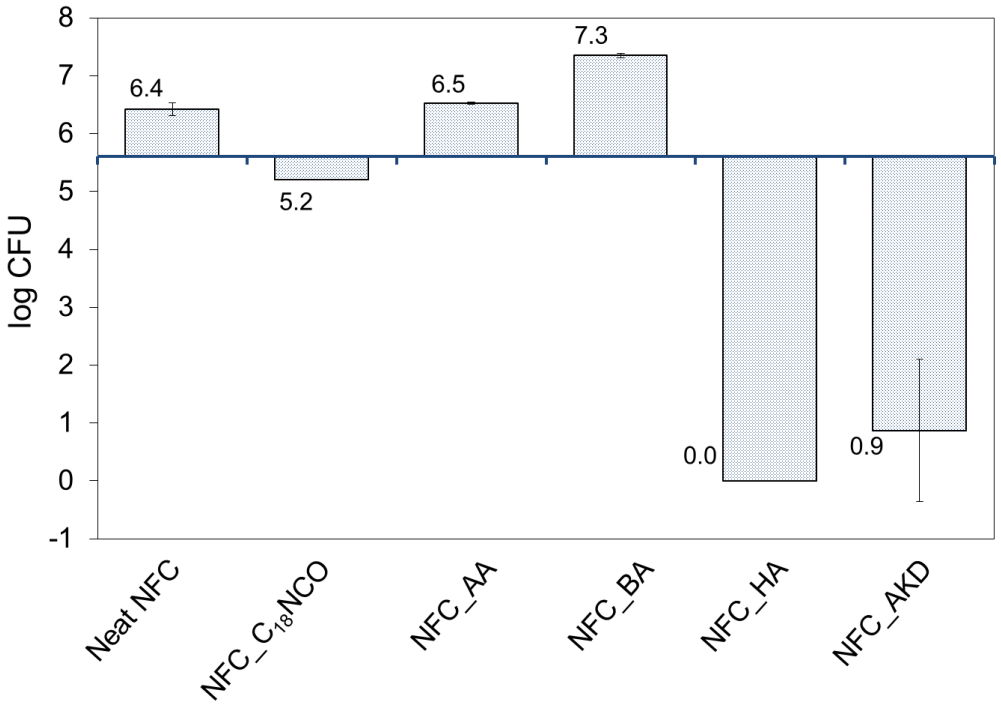

Figure 3-3 : Antimicrobial activity against *S.aureus* bacteria for neat NFC, NFC_C_{18}NCO, NFC_AA, NFC_BA and NFC_HA samples

On the contrary, NFC_HA shows a total antibacterial effect toward *S.aureus*. The length of the chemically grafted molecules plays an important role. Even if it is shorter than the NFC_C_{18}NCO, the density of hexyl chains in NFC_HA is higher, as reported in our previous

papers and confirmed by the contact angle data. It is known that fatty chains can destroy the cell wall of bacteria, which can explain this difference.

Finally the last sample tested was NFC_AKD. Only the antibacterial activity regarding *S.aureus* was performed. NFC_AKD test, represented in Figure 3-3, shows a high antibacterial activity reaching practically a total bactericidal effect. This might be due to the very long fatty chains at the surface, the slight presence of residual solvent but also to the presence of the surfactant used for this chemical grafting. Indeed release of surfactant can have anti-bacterial effect as previously showed with NFC treated.

As a conclusion, chemical grafting of NFC (comparing to neat NFC) can strongly improve anti-bacterial effect of NFC onto Gram positive bacteria if fatty chains are grafted.

The same protocol was applied on negative Gram bacteria i.e. *K. pneumoniae*. As presented in Figure 3-4, neat NFC causes a slight growth regarding *K. pneumoniae* while NFC_C_{18}NCO sample causes a weak reduction of bacterial growth for the same reasons involved regarding Gram+ bacteria (i.e. carbamate actions). Concerning the NFCs grafted with anhydride, NFC_AA sample shows a slight inhibition of bacterial growth in respect with neat NFC and no inhibition is assessed with butyric anhydride. Moreover, NFC_HA shows again the highest antibacterial effect toward *K. pneumoniae* in comparison to neat NFC. In this case, the log CFU decrease is less important proving that gram negative are less sensitive to fatty chain.

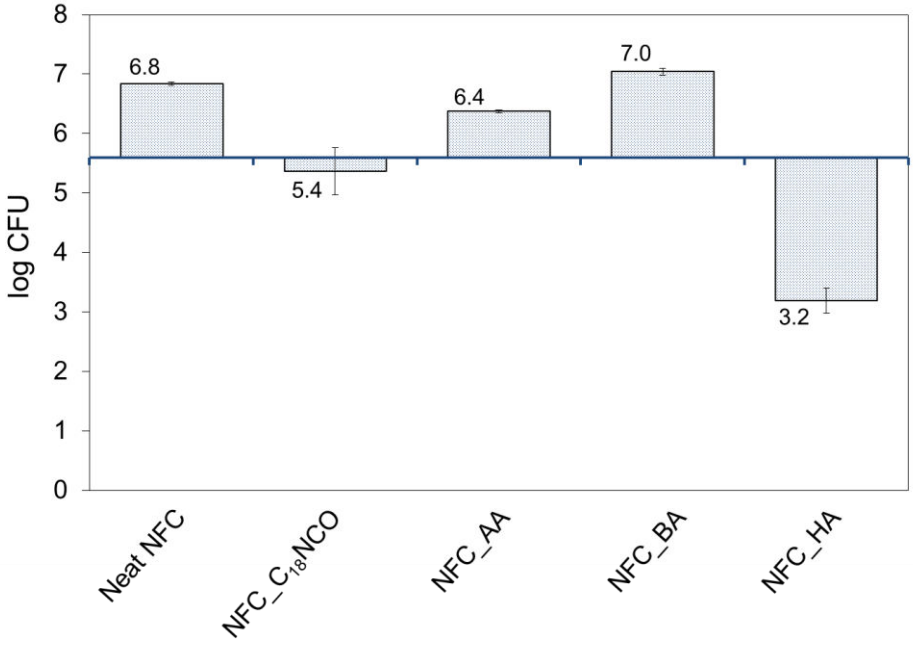

Figure 3-4 : Antimicrobial activity against *K. Pneumoniae* bacteria for neat NFC, NFC_C_{18}NCO, NFC_AA, NFC_BA and NFC_HA samples

Nevertheless, these first results are very promising and, even if other chemical grafting strategies should be tested, they confirm the possibility to provide anti-microbial effect to NFC by chemical grafting without any quaternary ammonium as previously tested (Andresen et al. 2007).

As mentioned before metallic nanoparticles like silver or TiO_2 usually are known to display effective antimicrobial properties. That is why; both chemical grafting and titanium dioxide nanoparticles adsorption on NFC were produced in this study in order to check if any synergistic action for bactericidal effect can be observed.

3.3.3 Antibacterial activity of grafted NFC functionalized with TiO_2

Neat and TiO_2 nanoparticles-functionalized NFCs have been used for comparative purposes. Indeed, the latter substrate displayed significant antibacterial effect as very recently reported by Martins et al. (Martins et al. 2012) in 2012 and confirmed again in Figure 3-5. TiO_2 particles are well known to generate free radical on the oxygen atom after a photo-catalytic activation, as discussed previously. The mechanism of antibacterial action of TiO_2 suggests that free radical of nanoparticles can interact electrostatically with anionic/cationic groups (depending on Gram+ or Gram-) at the bacterial cell walls causing an increase of membrane permeability and subsequent leakage of cellular proteins which ultimately leads to cell death. Also, photo-catalytic production of reactive oxygen species can damage DNA, cell membranes, cell proteins and may lead to cell death (Visai et al. 2011). However, one drawback is then the sensibility of cellulosic materials towards TiO_2 activation. One solution could be the protection of cellulose thanks to the chemical grafting as already shown with cellulose fibers.

NFC grafted with n-octadecyl isocyanate and then functionalized with TiO_2 nanoparticles, was then compared to neat NFC / TiO_2 as presented in the Figure 3-5.

The antibacterial effect is enhanced when TiO_2 particles are added to chemically modified NFC. Similar results are obtained with other chemical grafting. Regarding NFC_AA/TiO_2, NFC_BA/TiO_2 and NFC_HA/TiO_2 samples, they show higher antibacterial effect with respect to NFC_AA alone and NFC_BA which had almost no effect (as detailed in the previous section). Moreover, they achieved better results than neat NFC with TiO_2 particles. Contrary to what is expected, NFC_HA/TiO_2 is less effective than NFC_HA sample but display a significant bactericidal effect.

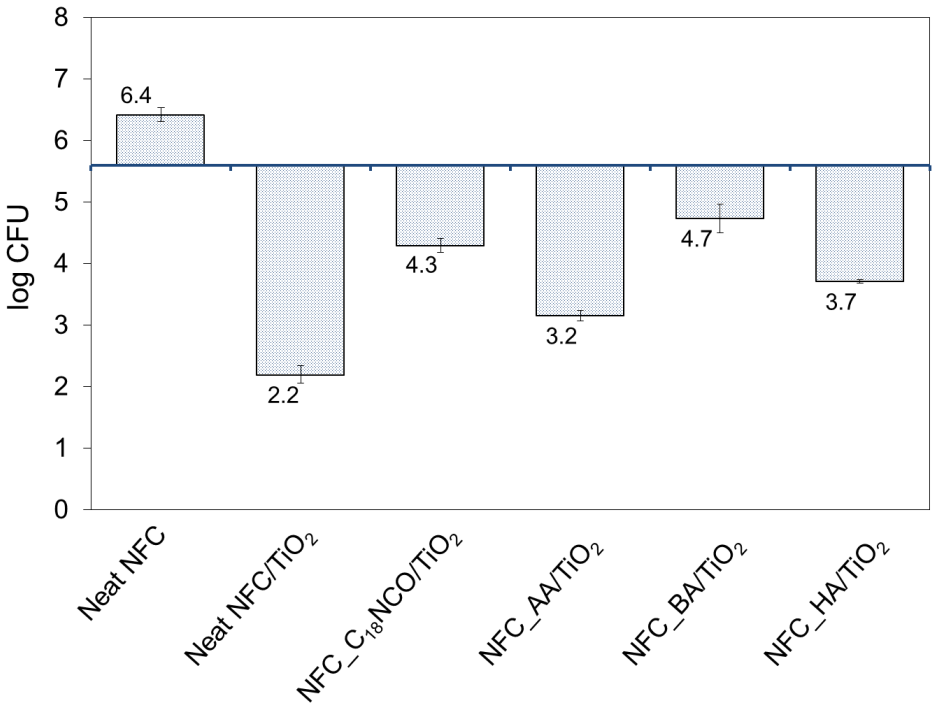

Figure 3-5 : Antimicrobial activity against *S.aureus* bacteria for neat NFC, NFC_C_{18}NCO, NFC_AA, NFC_BA and NFC_HA samples functionalized with TiO_2 nanoparticles

So the grafting of NFC enhanced the actions of TiO_2. This might be due to a synergistic effect or to a higher content of TiO_2 when NFCs are grafted.

In the case of the Gram- *K. pneumoniae* no significant differences are seen between native NFC/TiO_2 and NFC-grafted/TiO_2 samples, as summarized in Figure 3-6. Only NFC_BA/TiO_2 sample shows a higher antibacterial activity in comparison to the neat NFC/TiO_2 substrate. Unfortunately, the error scale bar is so high to come to an accurate conclusion. *K.pneumonia* bacteria seem to be less sensitive than *S.aureus* counterpart.

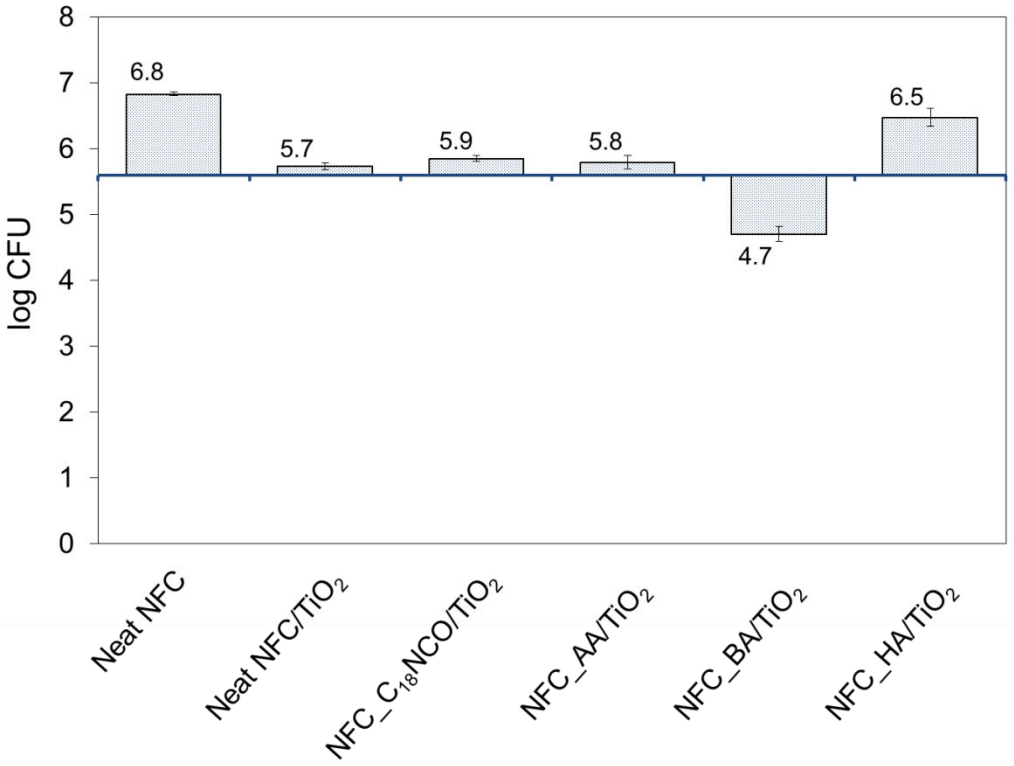

Figure 3-6 : Antimicrobial activity against *K. Pneumoniae* bacteria for neat NFC, NFC_C_{18}NCO, NFC_AA, NFC_BA and NFC_HA samples functionalized with TiO_2 nanoparticles

These results show that NFC treated with different grafts display at least a similar or a much better bactericidal effect than neat starting material. The chemical grafting reinforces microorganism killing effect of TiO_2 comparing to neat NFC. It could, therefore, be considered as a promising solution for achieving functional materials.

Modified NFC can display antimicrobial activity but cellulose material is also well-known to be biodegradable. The second part of this study is then dedicated to this behavior in order to check if the mechanism of biodegradability is altered by chemical grafting.

3.3.4 Biodegradability effect

As presented in the experimental section, the biodegradability was tested in aqueous environment. Neat as well as functionalized NFCs were tested. Mechanism of degradation of cellulose involves enzymes and specific activation keys. When the surface of cellulose is modified, the enzymes involved in the biodegradation need to adapt its key to be efficient. As shown in Figure 3-7, NFC_C_{18}NCO showed a slower biodegradation trend in comparison to neat NFC during the first 20 days. This behavior could surely be attributed to its hydrophobic properties limiting the accessibility at the beginning. Anyway the 90% biodegradation limit is reached within 45 days of test and even higher percentage of biodegradability is achieved at the end of the measurements. It is also well known that when carbamate functions are

involved, the biodegradability is enhanced and effective due to CO_2 release during carbamate functions hydrolysis (Cárdenas et al. 2002; Chapalamadugu and Chaudhry 1992; Chaudhry and Wheeler 2011).

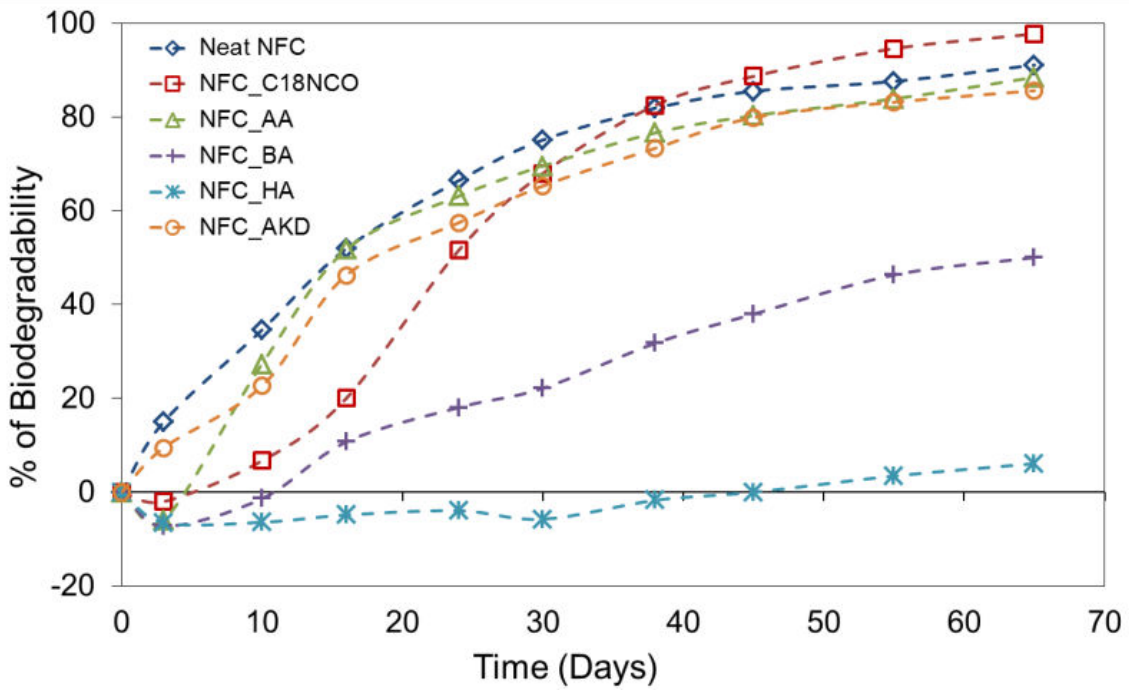

Figure 3-7 : Biodegradability curves for (a) neat NFC and NFC grafted using (b) NFC_C_{18}NCO, (c) NFC_AA, (d) NFC_BA, (e) NFC_HA and (f) NFC_AKD

For samples grafted with different anhydride moieties, the higher aliphatic chain is, the lower the biodegradability is. NFC_AA is biodegradable with a kinetic similar to neat NFC, whereas biodegradation kinetic of NFC_BA is lower than that of neat NFC. NFC_HA elements are not biodegradable. In fact, acetate molecules are needed for the development of enzymes/bacteria cellular material (DNA, membrane protein…). This phenomenon can explain the higher biodegradation rate obtained for NFC_AA. In the case of NFC_BA, the biodegradation rate is slow, and not enough to reach 90% in the limit period of contact test. It is clearly showed that kinetics are limited on this sample but not inexistent and may require longer contact time to reach 90% of biodegradation. Regarding NFC_HA, the sample is not biodegradable after the 65 days of tests. It can be linked to the higher hydrophobicity density (as described before). Enzymes had not found a good way during this contact time to adapt its degradation process in order to interact with grafted sample and degrade NFC.

The biodegradability of NFC_AKD obtained by nanoemulsion approach was confirmed with similar trend as neat NFC (Figure 3-7). The 90% biodegradation limit was nearly

reached within 65 days, by extending the testing time we can forecast that it could have been reached easily.

These results are very interesting because they proved that some samples like NFC_C_{18}NCO can be very interesting for their anti-bacterial effect meanwhile keeping positive biodegradability. Moreover such results show also that, by adapting the chemical treatment, we can monitor biodegradability of NFC samples and controlling its biodegradability as such or in final materials like composite or coated paper.

3.4 Conclusions

In conclusions, this paper shows very promising results for using chemically grafted NFC within high value added applications. Indeed NFC is already very innovative bio-based material which can strongly enhance mechanical or barrier properties of paper and composite. But this study proves that modified NFC can also be provided by anti-bacterial properties by keeping their biodegradability. Three kinds of chemical surface treatment were tested. Most of them allow achieving better anti-bacterial activity regarding gram+ or gram– bacteria, with even a synergistic effect when adding TiO_2 nanoparticles. Their biodegradability has been analyzed and is conserved, except for one which could be used as bio-based monitoring agent to control biodegradability of the final material. These first results are, therefore, very promising and should be completed by other chemical grafting and use of grafted NFC in final application. Nevertheless such study opens large spectra of research studies and applications within the field of functionalized NFC.

Acknowledgment

This research was supported by the "Scale-Up of Nanoparticles in modern PAPermaking" (SUNPAP) project of the seven framework program of European research under grant agreement n°228802. Authors want to thank all "SSCCP team" for their time in characterization.

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Figure captions

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General Conclusion

General Conclusion

The main objective of this work was to develop novel wood derivatives based materials. Indeed, current environmental concerns and increasing bio-based materials demands forced the Europe to support during these 3 last years the SUNPAP project, dedicated to up-scaling of NanoFibrillated Cellulose.

Concerning our contribution to this project, the main axe was to chemically modify nanofibrillated cellulose with new processes never used in literature and to check their possible use in some applications leading to added-value products.

As described all along the manuscript, NFC displays a lot of advantages like web like nano-structure and high potential reinforcement. Unfortunately, NFC still has some drawbacks that surface chemical modification could overcome. This is in line with our manuscript organization following three main chapters with firstly the understanding of this raw material, following by innovative chemical grafting of these substrates to finish by development of new applications.

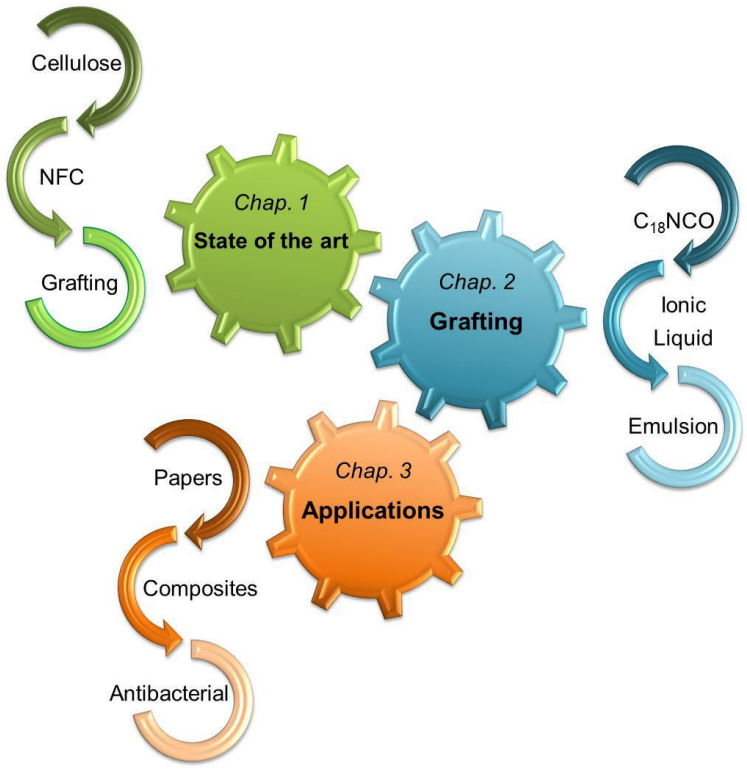

Figure 1 : Schematic representation of our project and its implementation

As represented by our project structure, the present research work was conducted in a progressive and structured way which can be divided in 9 parts. Our aim was not only to fix our effort on new processes for chemical modification but also on more fundamental comprehension of surface organization. Furthermore as a perspective, we studied several applications but also a way to easily dried and re-dispersed the NFC which is considered currently as the major drawback of NFC if scaling-up is performed.

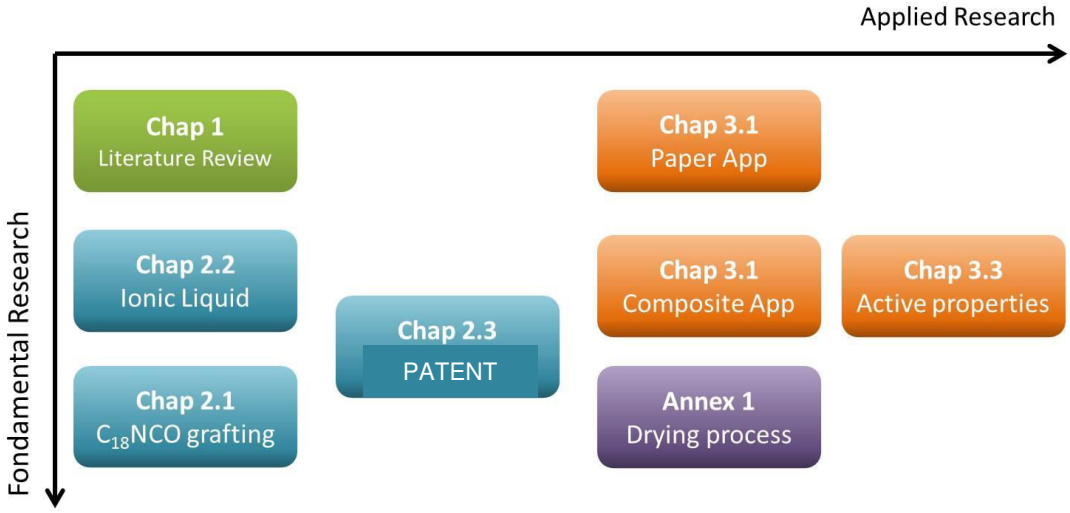

Figure 2 : Organization of the different parts constituting the manuscript

This organization and this strategy have enabled us to contribute to the field of NFC and their chemical modification by delivering key results and analyses whatever applied or fundamental researches is concerned (see Figure 2).

The first chapter, and more precisely the third part, was dedicated to a literature review of all chemical reaction performed on NFC. Listing the scientific papers before and after the start of the SUNPAP project proves the novelty of the topic with very small amount of strategies and exponential interest for such materials. Generally speaking, half of scientific papers available in literature have been published after the beginning of the SUNPAP project. This obviously proves the pioneer status of this study.

A clear need of modified materials is expected to overcome drawbacks occurred in different application. This third part should be published latter in a special issue of Material Reviews Journal (revision in progress) for updating our scientific groups.

Moreover, this first chapter was very useful for a better comprehension of chemistry of cellulosic particles; e.g. accessible hydroxyl group at the surface or the charges present at the surface. Moreover, when SUNPAP started, raw materials were not completely defined

and to enhance comprehension, we have studied rheology of several type of NFC suspension (not shown in this manuscript, conference TAPPI 2010). After the cellulose chemistry investigation, it was important to well understand what was feasible with NFC and not regarding chemical reactions depending on the type of NFC used (i.e. NFC enzymatically pretreated or TEMPO pretreatment). Clear charge determination was also proposed during the ACS CELL division 2012 (not shown in this manuscript).

The second chapter proposed three main ways to modify the surface chemistry of the NFC. The first one was to performed carbanilation on NFC based on a process developed in our lab with different amount of reagent comparing to hydroxyl groups available at the surface and their consequence on final properties. Surprisingly it proves the existence of an optimum link to the surface re-organization. Different chain length could be tested to confirm such organizations.

The second purpose was to use a non-volatile and easily recyclable solvent for the chemical reaction of NFC by using Ionic Liquid (IL) systems, which was never used for heterogeneous grafting. Promising results were achieved with anhydrides. Only surface grafting occurs as proved by innovative tool (TOF-SIMS) and hydrophobic NFC was produced. Such green process should be scaled up after investment for solvent (IL) purchasing. The process to have NFC suspension in IL should be also improved. One idea could be to use dried re-dispersible NFC as proposed as perspective in our patent and appendix 1.

The third part was dedicated to a development of a Water Based process for surface modification of NFC. Not all results are presented in this manuscript.

Never in literature such experiments were performed on NFC in order impart hydrophobic properties. At least 2 other strategies gave a new way to scientists for chemical surface modification of NFC.

The last step of our project consists in applying these modified NFCs in different application fields. Indeed, paper application using NFC modified with AKD was investigated in order to impart both hydrophobic properties bring by the AKD and in the same time improvement of mechanical properties of paper sheet provide by the addition of NFC. These objectives were successfully reached and for low content of modified NFC, we can produce hydrophobic paper sheets displaying a higher mechanical resistance and air barrier than paper sheets without NFC. This could be very useful for packaging applications for example.

The second field investigated was the use of NFC modified in ionic liquid systems within several bio-based matrices. In fact, three main matrices were tested. All of them were

cellulose derivatives (similar to grafted moieties at surface of NFC) and the objective was to have a better compatibilization between fillers (NFC or modified NFC) and the matrices. Results are promising: after the addition of NFC with only 10%wt. the thermomechanical properties are strongly improved. However chemical grafting only slightly improve properties (more homogeneous films) and several perspectives can be proposed to show their positive impact: gas barrier analyses, influence of post-thermoforming, extrusion process nanocomposite, and high quantity NFC nanocomposite.

The third application was dedicated to high value added application with characterization of active functionalities. Indeed, in this last part, the antimicrobial properties were checked for several grafted NFC (our 3 strategies). Some of chemical grafting had at least bacteriostatic or even bactericidal effect. This is very promising for packaging or medical paper applications. However this is the first time that such properties are reached with modified NFC. More fundamental studies and questions have to be targeted to understand the action of grafting on bacteria growth. What is very interesting is that similar strategies will be investigated during the next three years in new Marie-Curie project NewGenPack within our research team. Moreover biodegradability properties were also checked. The results are also very promising and in conclusion, we can monitor the biodegradability of NFC depending on the chemical grafting which can be very useful for some applications.

Regarding SUNPAP project, which would like a process able to be scaled-up, isocyanate chemical grafting was not adapted for a scale-up process due to the large amount of toxic solvent. Ionic liquid procedure was very promising but it needs a first high investment (not possible within this project). The difficulty to have NFC in IL suspension was also another reason why this strategy was not selected for production on a larger scale. Regarding NFC modified by AKD, it was possible to up-scale. So a proof of concept has been targeted and experimental devices have been designed during the second part of our study. Two trials with a 15L reactor batch were performed with enzymatically treated NFC. The ensued material, were not chemically grafted by thermal activation in order to be distributed to other partners of the project and be “activated” within their process.

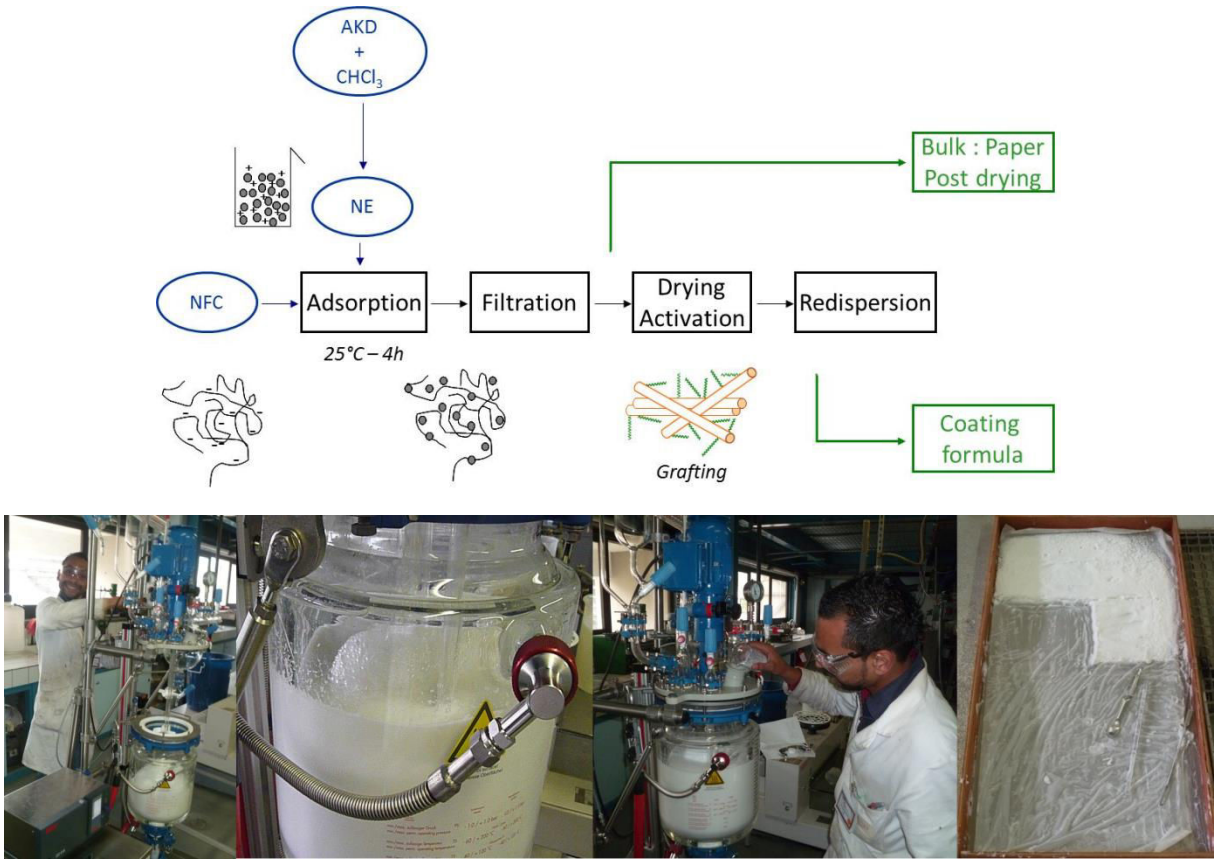

Figure 3 : Proof of concept for scaling-up of nanoemulsion based process

Several applications were tested with this material like use in foam coating at VTT (Finland), in packaging curtain coating at CTP (France), health and safety measurement at BIOSS (Finland), etc... Unfortunately some misunderstandings or other priority within trials limited understandable results. Only anti-microbial and biodegradability were promising. Moreover last results (detailed in our scientific) paper proved the interest of tempo-oxidized NFC. Unfortunately, not enough raw materials of tempo NFC were delivered, but for sure, it should be a clear perspective for this up-scaling strategy.

Furthermore, our experimental device has been used by other partners (University of Aveiro, Portugal) and as a conclusion; it allows us proving the feasibility of Nano-emulsion strategy up-scaling.

To summarize the contribution of this work to the field of NFC, it can be said that: t has brought:

(i) Important progresses and comprehension in chemistry of NFC by developing two new process for surface chemical modification

(ii) Promising solutions to impart hydrophobic properties and new functionalities in papermaking industry and composite applications

Numerous meetings and collaborations which have nourished our work were not reported here, for example writing of deliverable and milestones for SUNPAP project. Moreover, we participated to ACS meeting (Spring 2012) which was very useful to have a large view of the potential of NFC. Thanks to all meetings and people working on this field, NFCs seem to be very promising raw materials to produce high added-value products.

SUNPAP project and also our work was the first European project only dedicated on NFC production and modification.

As already explained, several perspectives can be listed and we have decided to propose you the most promising in Appendix 1. Indeed, a method was developed to dry and re-disperse NFC, which was impossible at the beginning of the project. This method was patented in June 2012 "Procédé de fabrication d'une poudre de cellulose fibrillée adaptée à être dispersée en milieu aqueux, Patent Number : FR12/55997" and can be very interesting for producers of NFC in order remove all water present in NFC suspension and have a huge gain in transport of this material. It can be also very useful for chemical grafting, avoid solvent exchanges procedures.

So, even if still lots of ideas are bumping as soon as new results are achieved, our study should help our scientific community with several published paper and congresses about innovative results and analyses.

We hope the present manuscript will contribute to (i) scientists which work on chemistry of these nanofillers and applications and (ii) attract more people coming from industry to be wowed by this material as we can be.

Appendix

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1. Water Re-dispersible Dried Nanofibrillated Cellulose

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Abstract

With ecofriendly perspectives in mind, the present study reports for the first time a method to obtain water re-dispersible dried NFC using freeze-drying. No chemical surface modification was required to get this kind of products. Salt addition (NaCl) strategy has been selected to block and then to regenerate hydrogen bonds during the drying and the re-dispersion steps, respectively. Several samples were produced at different pH (i.e. 4, 6, 8 and 10). All the re-dispersed NFC were characterized by different techniques (e.g. FE-SEM, XRD, EPMA-EDX) to check the effect of salt on NFC aggregation. The interactions between NFC and sodium chloride at different pH conditions have been discussed and the rheology of the re-dispersed NFC suspension has been performed. All the results prove a perfect water re-dispersion at pH 8 and exactly similar suspension is obtained after water dispersion of dried NFC following our procedure. These results are very promising for increasing application of NFC.

Keywords

Nanofibrillated Cellulose – Freeze-drying – Water re-dispersible – Salt

***Inspired from**: Karim Missoum, Julien Bras, Naceur Belgacem – Biomacromolecules (2012) – Accepted*

1.1 Introduction

Cellulosic material has been studied and applied for a while thanks to its abundant production by photosynthesis and its particular properties. Since the last decade nanocelluloses know a great interest, as witnesses the appearance of more or less one scientific paper every day. Two kinds of nanocelluloses are usually available. The first one is obtained from a hydrolysis of cellulose fibers to collect NanoCrystalline Cellulose (NCC or whiskers) (Habibi et al. 2010; Klemm et al. 2011; Siqueira et al. 2009), whereas the second is produced after a mechanical disintegration of cellulosic fiber pulp through a high-pressure homogenizer (Siqueira et al. 2009; Klemm et al. 2011; Pääkkö et al. 2007) and called micro or NanoFibrillated Cellulose(NFC). This study deals with the second type (NFC), whose preparation was firstly achieved in 1983 by Tubark et al. (Turbak et al. 1983) and Herrick et al. (Herrick et al. 1983). Since that time, nanofibrillated cellulose was widely investigated and used in several applications with very outstanding and promising impact as explained by recent reviews or books (Belgacem and Gandini 2009; Mohanty et al. 2000; Siró and Plackett 2010). Several pre-treatment on cellulose fibers can be also applied before mechanical shearing such as enzymatic (Pääkkö et al. 2007; Siró and Plackett 2010; Siqueira et al. 2010c) or chemical pretreatment (Isogai et al. 2011; Saito et al. 2007). This creates new families but also reduces the energy consumption and facilitates the preparation of NFC announced as industrially available in 2012.

However, the hydrophilic nature of cellulosic limits their applications such as coated products (Lavoine et al. 2011) or within composites (Siró and Plackett 2010; Hubbe et al. 2008; Siqueira et al. 2010d; Siqueira et al. 2010b; Kaith and Kaur 2011; Eichhorn et al. 2010) due to two main drawbacks: (i) they generally are high viscous aqueous suspension at low solid content and (ii) they undergo irreversible aggregation once dried (films or powder). This is mainly due to the capacity of NFC to form hydrogen bonds between these high specific area nanofibers. Moreover, hornification phenomenon during drying, reported by several authors (Hult et al. 2001; Iwamoto et al. 2008; Young 1994), reveals the formation of additional hydrogen bonds between amorphous parts of the cellulosic nanofibers, thus contributing to the aggregates irreversible formation. In addition, more stable hydrogen bonds are formed during drying and cannot be “broken” after re-wetting. In order to overcome this drawback, different solutions were studied, but the most developed one is the surface chemical modification (Gandini and Belgacem 2011; Krouit et al. 2008; Lonnberg et al. 2011; Pahimanolis et al. 2011), which aims at transforming hydroxyl groups borne by cellulose macromolecules at the surface of NFCs into other functions thus limiting (or even

totally avoiding) the hydrogen bonds establishment thanks to esterification (Missoum et al. 2012a; Stenstad et al. 2008), carbanilation (Siqueira et al. 2010a) etc... Nevertheless, such solutions are difficult to up-scale and costly affects the ensuing NFC. However, the fact that it is not possible to use them at dry state without tendency to form irreversible aggregates or even film-like material strongly limits their transport and their applications.

To the best of our knowledge only very few studies proposed a solution of getting dry non aggregated NFC. Eyholzer et al. (Eyholzer et al. 2010) have reported, for the first time in 2010, the preparation of NFC powder by carboxymethylation of the initial substrate. Unfortunately, this strategy corresponds to a chemical treatment of NFC. At the end of 2011, a spray drying strategy has been proposed for the drying of nanocellulose (Gardner et al. 2011; Peng et al. 2012). A powder can be obtained using this strategy but the authors have not discussed clearly about the possibility to re-disperse the NFC powder in water and the preparation of aggregates-free NFC suspensions.

Similar problems have been encountered when working with cellulose nanocrystals and solved thanks to an invention developed and patented very recently by FP innovation (Beck et al. 2009). Thus, dried NCC re-dispersable powder is now available within CelluForce JointVenture. However, the charge density and its chemical nature are totally different between NCC (i.e high amount of SO_3^-) and NFC (low amount of $-COO^-$). This feature is due to the differences in the isolation process. In fact, NCC arises from sulfuric acid hydrolysis which induces the grafting of sulfate groups of the surface, whereas NFC are mechanically isolated and their charge originates from carboxylic groups of initial raw material (borne by hemicelluloses) or formed by TEMPO pretreatment. Moreover, NFC entanglement (much higher aspect ratio than NCC) completely changes the process of drying and re-dispersing. That is why the present work proposed a novel method to dry NFC by keeping them easily water re-dispersible using a mechanical dispersion. Thus, for the first time, dried NFC particles are obtained without any chemical surface modification or adsorption, but only by adding a hydrogen bond blocker in the suspension before drying. Morphological, structural and rheological characterizations were performed before and after drying and re-dispersion. Influence of pH was also investigated.

1.2 Experimental

1.2.1 Materials

Sodium chloride (NaCl) salt, hydrochloric acid (HCl) and sodium hydroxide (NaOH) normadose were supplied from Aldrich (France). Dialysis membranes (Spectra/Por3 3,500 Daltons) were purchased from SpectumLabs (USA). Deionized water was used in all experiments. Bleached wood pulp was kindly supplied by Domsjö (Finland).

1.2.2 NFC production

Nanofibrillated cellulose suspension was produced from Domsjö pulp. A suspension of bleached Domsjö fibers (2.0%wt.) was enzymatically pretreated with endoglucanase (Cellulase) during 1h at 50°C. Then, the slurry was fibrillated using a Masuko Grinder© (Japan). Size reduction of the fibers into nanofibrillated cellulose was obtained after 10 passes between the rotating and the static stones at 1,500 rpm. Solid content of the NFC suspension is around 2.6% (w/w), which gives systems with optimal viscosity level.

1.2.3 Scanning Electron Microscopy (FE-SEM)

A scanning electron microscope equipped with a field emission gun (FE-SEM), model Zeiss Ultra column 55 gemini, was used to observe NFC. The accelerating voltage (EHT) was 3 kV for a working distance of 6.4 mm. A droplet of diluted suspension was then deposited onto a substrate covered with carbon tape and coated with a 2 nm layer of Au/Pd (Gold/Paladium) to ensure the conductivity of all samples.

1.2.4 Electron Probe MicroAnalysis (EPMA)

In order to characterize the NFC and the salt added in the aqueous suspension, microscopy analyses were performed using a SEM coupled with an EDX (Energy Dispersive X-Ray) detector, in order to track NaCl distribution on the sample surface. To perform analyses, a voltage of 15 kV combined with a low vacuum ($5.6x10^{-4}$ Torr) were applied. One scan is performed during 0.971s during 60s. One drop of each suspension was deposited on a carbon tape substrate.

1.2.5 X-Ray Diffraction (XRD)

The (wide-angle) X-Ray Diffraction analysis was performed on freeze-dried NFC powder containing or not NaCl. The samples were placed in a 2.5mm deep cell and measurements were performed with a PANanalytical, X'Pert PRO MPD diffractometer equipped with an X'celerator detector. The operating conditions for the refractometer were: Copper Kα

radiation (1.5418 Å), 2θ (Bragg angle) between 5 and 60°, step size 0.067°, counting time 90s. The degree of crystallinity was evaluated using the Buschle-Diller and Zeronian Equation (Equation 1) (Buschle-Diller and Zeronian 1992) :

$$I_c = 1 - \frac{I_1}{I_2} \qquad \text{Eq. 1}$$

Where: I_1 is the intensity at the minimum (2θ = 18°) and I_2 the intensity associated with the crystalline region of cellulose (2θ = 22.5°). All measurements were made at least in duplicates.

1.2.6 Rheology measurements

Rheological measurements of aqueous NFC suspensions were carried out using a controlled stress rheometer (MCR 301, Anton Paar Physica, Austria) calibrated and certificated, with a parallel plate fixture (diameter 25mm with gap of 1mm) at 20.0°C, controlled by a Peltier system. A glass solvent trap was used to prevent water evaporation. Flow curves were plotted from the corresponding transient tests (apparent viscosity, η(Pa.s), *vs*. time at constant shear rates, γ (s^{-1})), in a wide range of shear rates, i.e. from 0.001 to 10 s^{-1}. Flow curves were carried out in duplicate, for each tested storage time.

1.2.7 Water content measurements

The water content was determined after a drying in an oven at 100°C during 4h to ensure the total evaporation of water present in the samples. The weight was left to reach constant value for each water content determination. Each measurement was replicated three times and gave for each sample a solid content of 98%.

1.2.8 Preparation of dried NFC powder and redispersion

The NFC suspension at 2% is diluted by adding 100mL of distilled water, before acidification of the medium (by adding HCl solution at 0.1M), in order to decrease the pH to 2.8. This operation allows getting the H-NFC form and starting with the same pH for all suspensions. Then, sodium hydroxide solution is added to reach a pH value of 4, 6, 8 and 10. The quantity of the added NaOH is very low, which avoid impacting the ionic force of the system. All suspensions were freeze-dried in the same conditions, i.e. 2 days at -81°C under a pressure of 0.18mbar, with a freeze-drying apparatus. Each powder got after freeze-drying was re-dispersed in distilled water to reach a concentration of 1%wt. using Ultra-Turrax T25 device. The mechanical shearing is applied during 30 seconds.

1.3 Results and Discussions

The main target of this study is to obtain water re-dispersible NFC after a drying, in order overcome the drawbacks limiting the use of NFC in several fields of applications and facilitate their transport. For achieving such a target, the selected chemical should avoid (or at least limit) hydrogen bonds but also be easily dissociated from NFC after re-dispersion for retrieving their hydrogen bond linked to their properties.

1.3.1 Dried NFC powder

It is well known that NFC have some charges at their surface (Wågberg et al. 2008; Wågberg et al. 1988; Wågberg et al. 1987) due to the carboxylic groups present in hemicelluloses macromolecules (Iwamoto et al. 2008). These groups (-COOH) positively influence inter-NFC hydrogen bonding. Masking such moieties could limit the aggregation of the NFC. COOH groups (pK around 8.5) display labile hydrogen. Thus, adjusting the pH value of the aqueous suspensions would yield to the carboxylate form. The quantity of the added NaOH is very low, which avoid impacting the ionic force of the system. The ensuing negatively charged particles will repulse each other, thus producing improved dispersed NFC^-. Adding monovalent cation (X^+) and drying the resulting suspension will produce X^+-$^-$ NFC form, which should limit the formation of hydrogen bonds during the drying process and make easy the re-dispersion of the dried NFC.

Sodium chloride was used to obtain Na^+ as counter-ion due to the easy dissociation of this salt in water whatever the pH. Different samples were also prepared and characterized, as illustrated by Figure 1-1. Actually, three different parts of each suspension were isolated. The first one is freeze-dried suspensions without NaCl, corresponding to reference system at different pH and identified as NFC 1. The second part (NFC2) is separated at different pH with an ionic strength of 10mM controlled by the addition of NaCl salt into the slurry. The third part (NFC 3) corresponds to NFC 2, which was submitted to dialysis during 24h using a membrane to remove the salt present in the suspension. The three samples were then characterized.

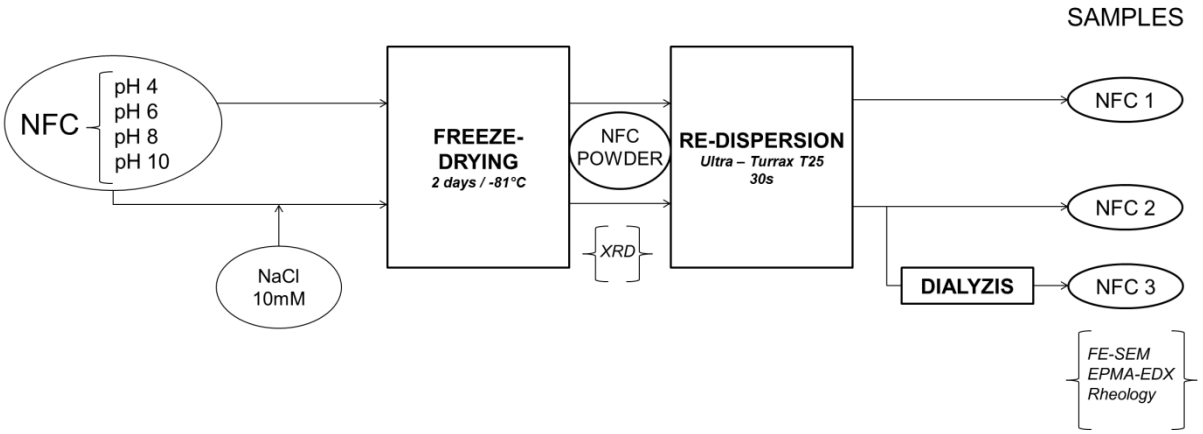

Figure 1-1 : Process for drying NFC using freeze-drying device

Pictures of the different suspensions and powder obtained are summarized in Figure 1-2, which represents the treated and untreated NFC (at different pH) after re-dispersion in water. These photos exhibit clearly the effect of salt (added before drying) on the stability of the final aqueous suspension. After 30 seconds, the suspension obtained from the NFC1 is unstable, i.e. a sedimentation effect is observed, whereas the NFC2 is still well dispersed and stable after 3 months.

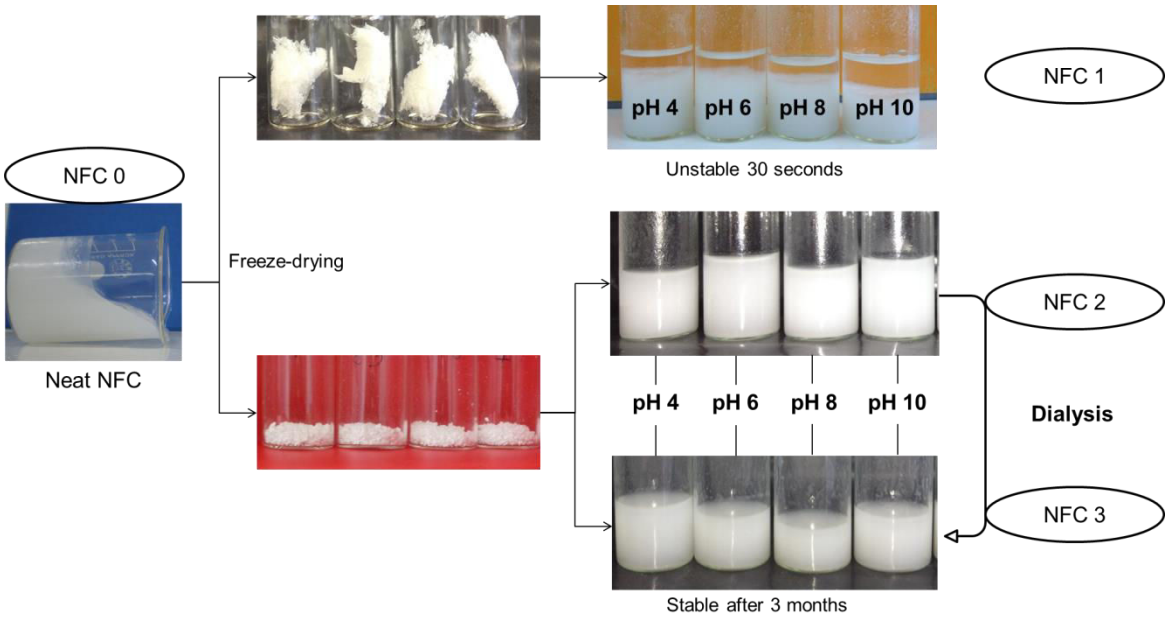

Figure 1-2 : Pictures of the different samples obtained for each sample

The dimensions of different NFC (dried and re-dispersed) have been analyzed by electron microscopy. The investigation of the reference sample (NFC 1) (i.e. same treatment as the other samples but without NaCl salt addition) is presented in Figure 1-3. At low magnification,

it shows the presence of aggregates whatever the pH value. This is due to formation of hydrogen bond at different pH and non-uniform re-dispersion by mechanical treatment.

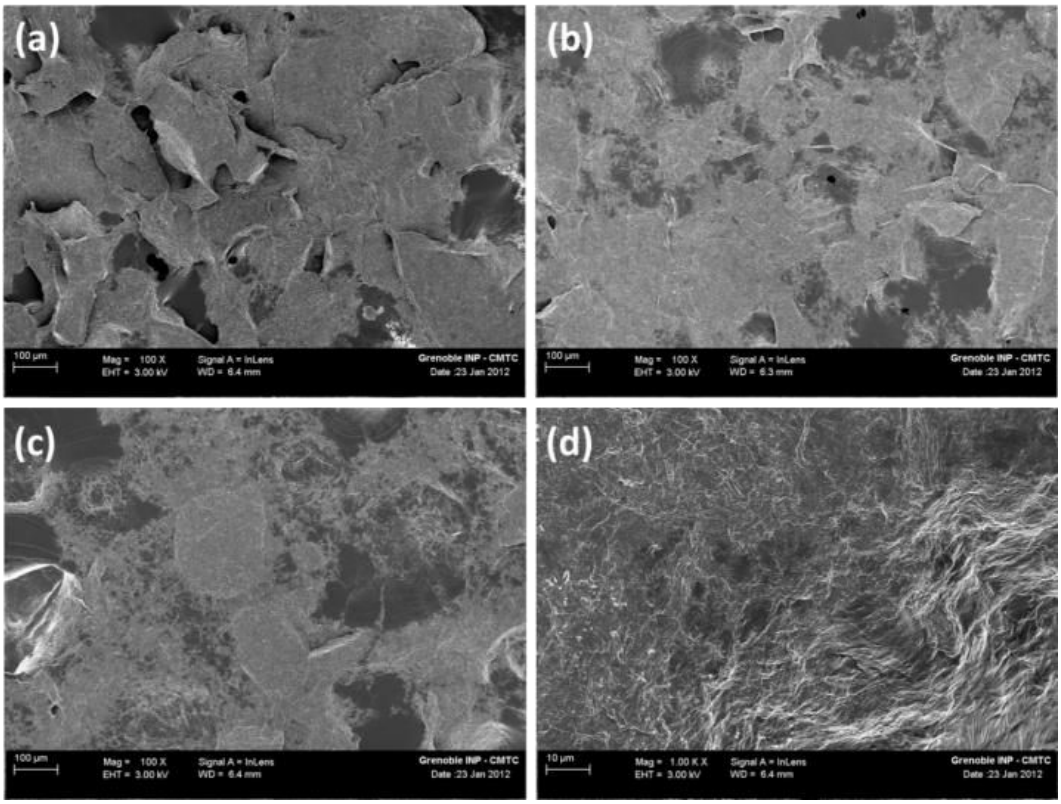

Figure 1-3 : FE-SEM pictures for samples of dried NFC 1 at (a) pH 4, (b) pH 6, (c) pH 8 and (d) pH 10

Regarding NFC2, FE-SEM characterizations, presented in Figure 1-4, show a more homogeneous macro-structure (at 200µm scale), in comparison to the previous samples (NFC1). Deeper analyses at nano-scale point out clearly the presence of salt but also the conservation of the nanometric dimension of NFC with a diameter around 23 +/- 8nm, independently from the pH value. This value is completely similar to that observed for neat NFC (not shown) of 22 +/- 6nm, which suggests that no aggregation has occurred and proves the positive effect of NaCl addition in the suspensions acting as hydrogen binding blockers. However, salt is still present even if, qualitatively, it seems that NaCl crystals are less present for the sample with a pH of 8 (see white dots all around the dried drops in Figure 3).

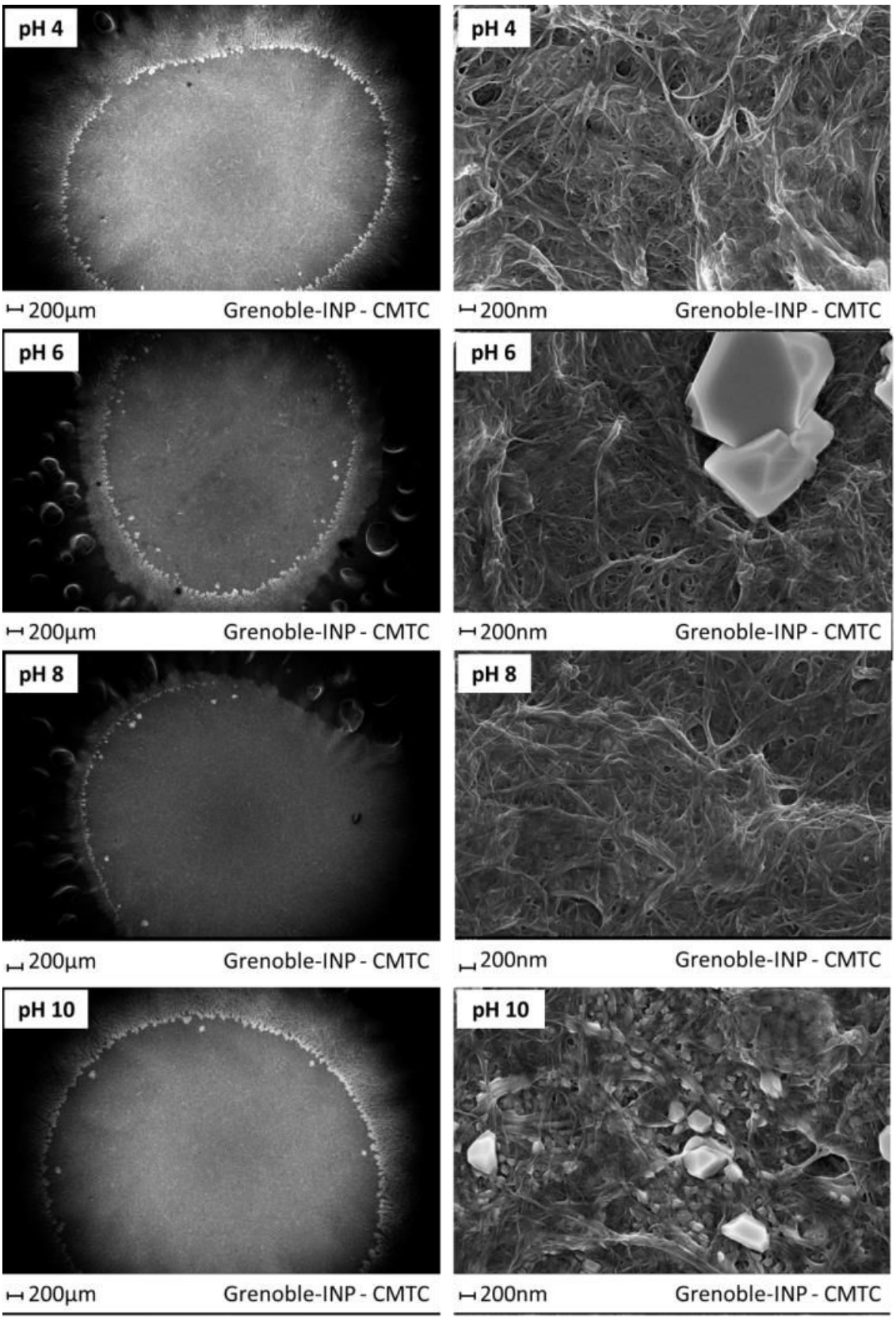

Figure 1-4 : FE-SEM pictures at macro-scale (left) and nano-scale (right) for samples of NFC 2

Figure 5 shows micrograph obtained, by FE-SEM analyses, after dialysis (NFC 3). The nano-scale is well conserved with an average diameter around 21 +/- 9nm. Moreover, after 24h of dialysis, no residual NaCl salt is observed by EPMA-EDX.

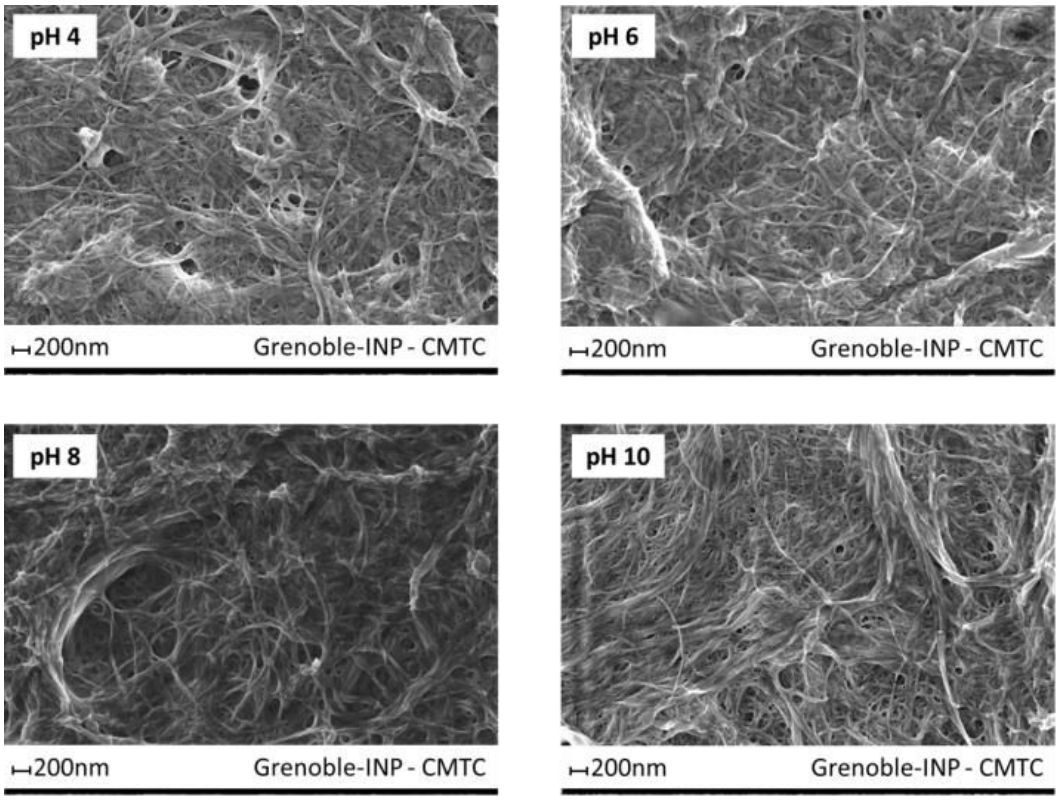

Figure 1-5 : FE-SEM pictures characterizing samples from sample NFC3 after dialysis

Concerning structural properties, Figure 1-6 summarizes the different patterns obtained thanks to X-Ray Diffraction measurements of NFC2. It confirms that all samples have similar properties in terms of crystallinity index whatever the pH and the drying process. Indeed the crystallinity index of cellulose is not affected by the presence of NaCl in the media. Thus, Ic was found to be 75% for the reference (NFC1) and 74% for NFC2 with salt. For the other samples, values of 74.7%, 74.3%, 74.0% and 73.0% were measured for samples from NFC2 with pH equal 4, 6, 8 and 10, respectively, which proves that pH does not influence NFC structure. The presence of NaCl salt in the suspension was detected through the characteristic peaks at 2θ = 26.9°, 36.1°, 45.2° and 55.7° corresponding to (111), (200), (220) and (222) Miller indices respectively.

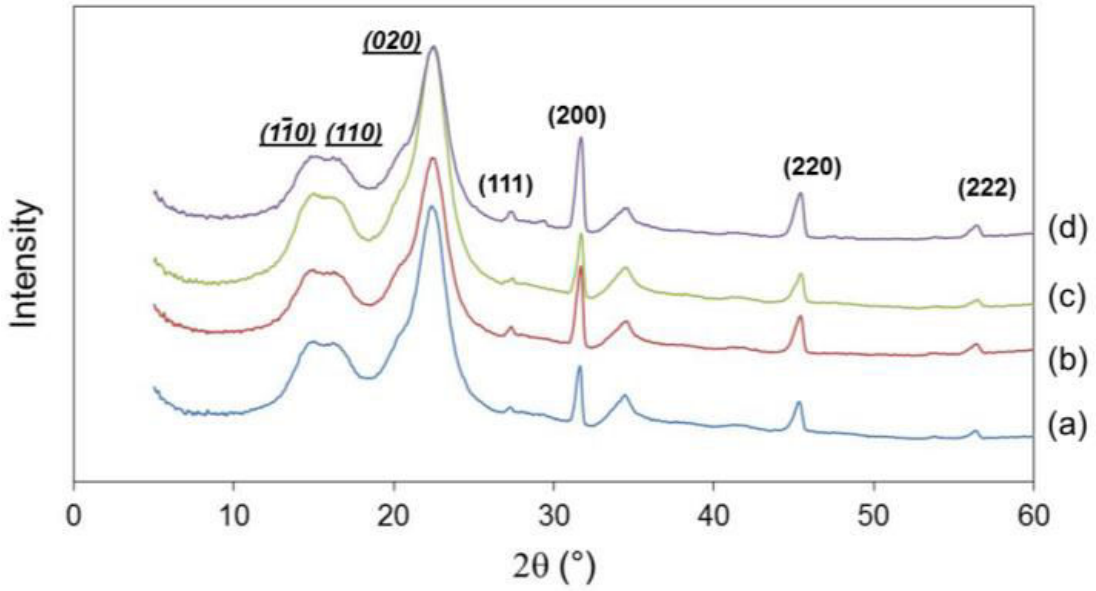

Figure 1-6 : X-Ray diffraction patterns and for samples obtained from sample NFC2 for (a) pH 4, (b) pH 6, (c) pH 8 and (d) pH 10

In conclusion, the crystalline structure was not altered and the quality of crystals presents in NFC is roughly the same. Thanks to FE-SEM characterization, the nano-scale size is conserved for all the freeze-dried in the presence of NaCl samples, re-dispersed and dialyzed. Deeper investigations for the mechanism of interaction between the salt and NFC were performed using an EDX system.

1.3.2 Semi-quantitative characterization by EPMA-EDX

As already mentioned, cellulose nanofibrils display some charges at their surface due to the presence of residual hemicellulose attached to the cellulose macromolecules. These hemicelluloses are mainly glucomanane type for softwood. Based on the pKa data of carboxylic groups, the carboxylate form can be obtained from a pH higher than 5. The totality of carboxylate groups is obtained for a pH value around 7-8. For instance, the carboxymethylcellulose can precipitate in neutral conditions and be well dispersed in basic aqueous media. In the present work, EPMA-EDX studies of the samples can be a good way for a qualitative determination of an optimal pH value. Indeed theoretically, the maximum complexation between carboxylate groups and Na^+ ions reached for a certain pH will also be the best solution for blocking this kind of hydrogen bonds. The EPMA-EDX device can follow the proportion of an atom with an atomic number strictly superior to 11 in their non-ionized state. The relative quantity of carbon is more or less the same in all NFC samples whereas the relative quantity of non-ionized sodium would be different for different pH conditions due

to the complexation effect. Thus, an “index of non-complexation” between carboxylate groups and Na^+ ions can be determined using the ratio I_{Na}/I_C for each pH values and with the assumption that similar ratio of NaCl/NFC has been used during mixing. When the value is high, there are more Na atoms detected, indicating that there is a higher amount of free Na^+ cations. The Table 1-1 and Figure 1-7 summarize all data obtained for NFC2and NFC3 (dialyzed materials) samples.

Table 1-1 : Intensity value of detected atom using EPMA – EDX. Determination of complexation index

Samples		I carbon	I sodium	I chlore	I_{Na} / I_C	I_{Cl} / I_C
NFC 2 Non - dialyzed	pH 4	1346	116	170	0.086	0.126
	pH 6	1402	70	106	0.050	0.076
	pH 8	1494	26	27	0.018	0.018
	pH 10	1454	192	279	0.132	0.192
NFC 3 Dialyzed	pH 4	1300	31	43	0.024	0.033
	pH 6	1387	24	34	0.017	0.025
	pH 8	1386	22	33	0.016	0.024
	pH 10	1414	42	77	0.030	0.054

Figure 1-7 presents the non-complexation index (I_{nc}) of the investigated samples and shows that the Na-NFC form seems to have the lowest value (considered as optimal in our case), for a pH around 8. First, at pH 4, no carboxylate groups are available and therefore no complexation can take place. It characterizes NaCl added in the solution, which have not been exchanged as counter-ion. At pH 6, few carboxylate groups are available, thus inducing some complexation events, which explain the diminution of the index under scrutiny.

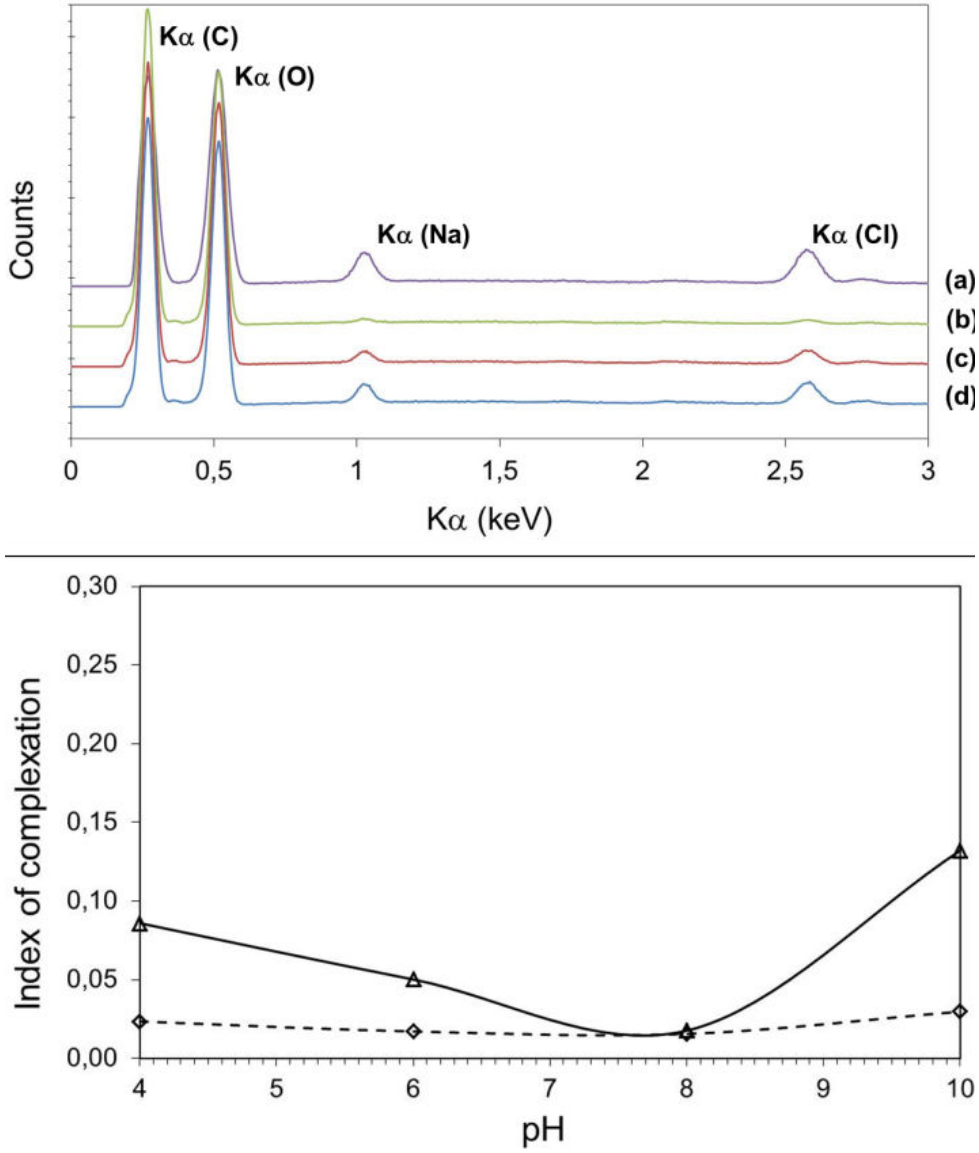

Figure 1-7 : EPMA-EDX analysis obtained for NFC2 at (a) pH4, (b) pH6, (c) pH8 and (d) pH10 (top) followed by the index of complexation curves function of the pH obtained from ratio Na/C for samples of NFC 2 (plain line) and NFC 3 (plotted line)

The optimal pH value for complexation is obtained at pH 8, as expected from the pKa values of these groups. Thus, at this pH range, most of carboxylate groups are available and consequently the maximum of complexation can be reached. Indeed, the "index of non-complexation" at this pH is close to zero. At pH 10, the index value increases. All chloride ions from NaCl are associated with sodium ions (Na^+) coming from the excess of sodium hydroxide (NaOH) solution added to regenerate NaCl salt. In conclusion, minima obtained in the I_{nc} curves and the optimal complexation is determined for a pH around 8, which correspond to the highest amounts of carboxylate functions screened by the Na^+ ions.

Moreover, ion-dipole interactions play an important role in such phenomena, as in the case of salts dissolution in polar solvents (e.g. NaCl in water). In these cases, the free energy required to disrupt the strong attraction between solute particles is supplied mainly by the charge-dipole interaction between the solute particles and the solvent molecules. It is well-known that cellulose display a permanent dipole induced by the hydroxyl groups, which could be comparable to water interactions. The number of hydrogen bonds, which are formed during drying of cellulose particles, can be strongly reduced thanks to ion-dipole interactions when NaCl is added, as shown in Figure 8. Indeed, in water, the dissociation phenomena can give Na^+ and Cl^- ions. Na^+ can easily interact with the $2\delta^-$ of Oxygen atom present in cellulose (cf. Figure 1-8), whereas Cl^- enters in interactions with δ^+ of Hydrogen atoms directly linked to the previous Oxygen atom. Consequently, the hydrogen bond formation in cellulose are blocked (screening effect) when it is dried. These ion-dipole interactions cannot be broken after freeze-drying of our substrates. However, these kinds of interactions are not strong enough to impede the re-dispersion of the NFCs. In fact, the formed charge-dipoles at dry state can be easily removed when polar solvents (water, for instance) is added again.

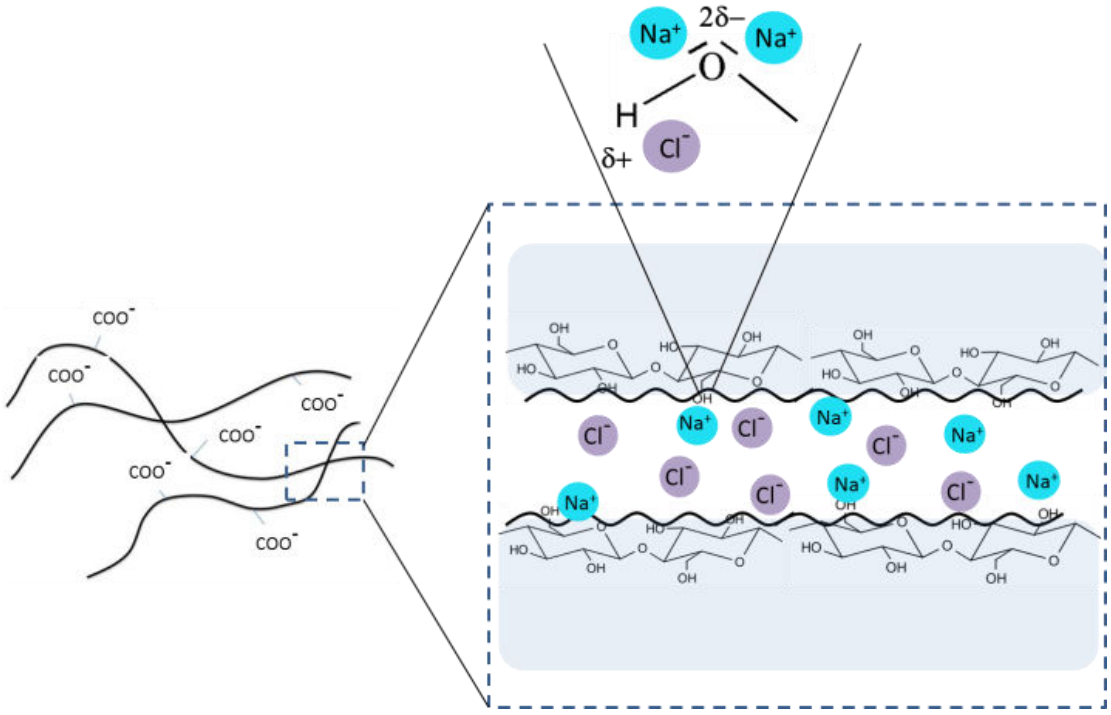

Figure 1-8 : Ion-dipole interactions between nanofibrillated cellulose and NaCl salt at acting as "hydrogen bond blocker"

In comparison to the patent on dried NanoCrystalline Cellulose, developed by FP Innovation (Beck et al. 2009), only the re-dispersion in different aqueous solvent was performed to check the best condition to re-disperse the NCC. A very recent scientific publication paper (Beck et al. 2012) gives much more details on the process in order to dry and re-disperse NCC without agglomeration. As said before, NCCs are rigid particles in comparison to NFCs that are more flexible, longer material and display entanglement ability. That is why mechanical shearing step for re-dispersion of NFC is necessary as the sonication step to obtain individual colloidal suspension of NCC. Moreover, in the case of NCC, a large amount of sulfate group (SO_3^-) is present at their surface and constitutes the main reason for salt adsorption. Indeed the re-dispersion is effective whatever the pH due to the low pKa value of HSO_3/SO_3^- couple. After the screening by the salt on the anion form of NCC, it is impossible to form hydrogen bonds, during drying step, which are responsible of aggregation. In our case, there are two main phenomena, the content of carboxylic group present on NFC and the ion-dipole interactions between hydroxyl groups of cellulose and the salt as described before. In conclusion, mechanism involved to avoid aggregation is completely different regarding NCC and NFC. Our study is still very innovative and promising as proved by our patent application (Missoum et al. 2012b). Indeed this study emphasizes the increase of ion-dipole interactions linked to the high specific area of NFC.

In the previous scientific publications about dried NFC, characterizations of physical properties were not performed after NFC re-dispersion to be sure that treatment does not altered them. In our study, rheological behavior was checked to ensure the good re-dispersion of NFC and the impact on viscosity before and after removing salt from the re-dispersed suspension in comparison to a reference.

1.3.3 Rheology measurements

As explained, the idea is to limit hydrogen bond during drying but also “regenerate” these OH bond once NFC have been re-dispersed to achieve similar properties between never dried NFC and dried NFC. Rheology could help to check this point. Indeed neat NFC suspension has high viscosity at very low concentration. Theoretically, the higher is the viscosity the more cohesive is the gel. In such a case, the hydrogen bond concentration is also higher. Moreover, rheology measurements can be also helpful to check the aggregation effect. The higher is the aggregation, the stronger are the hydrogen interactions, and consequently the lower is the suspension viscosity. As presented in Figure 1-9, all the investigated suspensions present the same rheo-thinning behavior. For samples of the NFC1 (without salt), the viscosity is different and it is function of the pH and shear rate values. This

observation can be correlated to the amount of the aggregates formed during the drying of NFCs, as shown in Figure 2. However, all the samples from NFCs 2 – 3 (b/c graphs) behave similarly whatever the pH value.

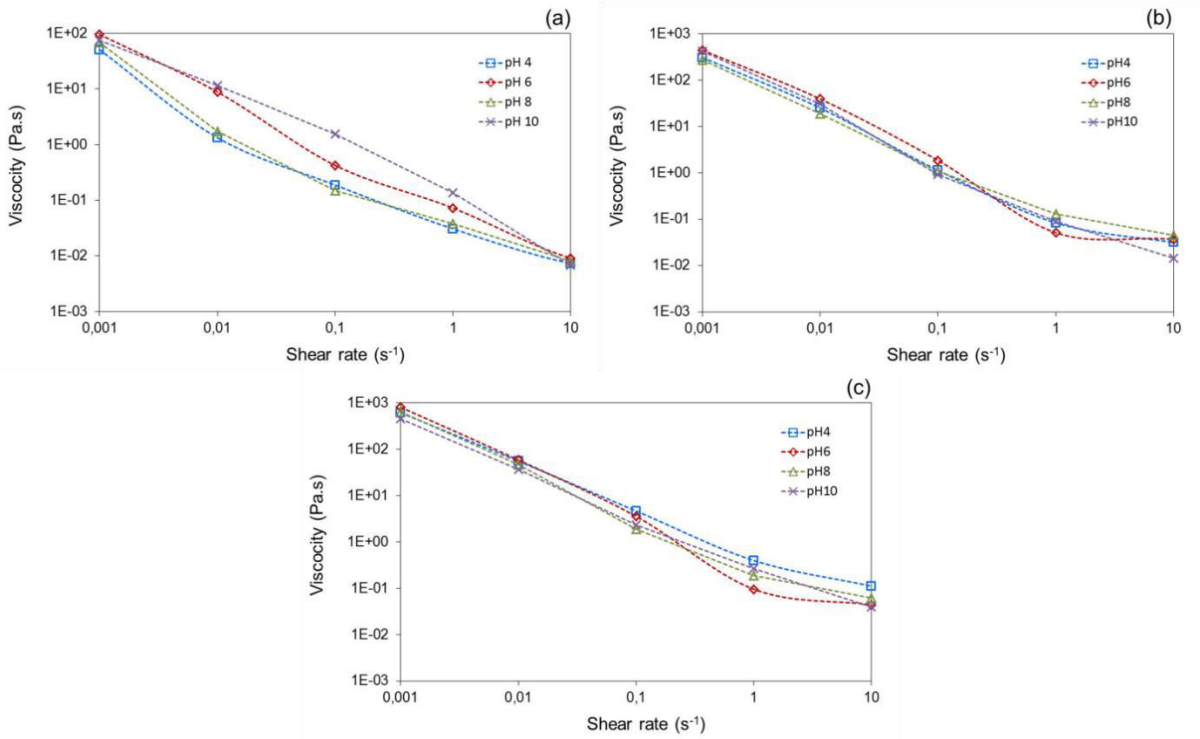

Figure 1-9 : Rheology curves – viscosity function of shear rate for sample of (a) NFC1, (b) NFC2 and (c) NFC3

Figure 1-10 shows clearly the effect of NaCl addition on the rheological properties during the freeze-drying process. For pH 4, the viscosity decreases in the order of NFC3, NFC2, and NFC1, respectively. The salt addition induces a rheo-thinning behavior for the studied suspensions, which allows obtaining a more fluidic system. The strong diminution in viscosity concerning the sample from NFC1 is due to the agglomeration and aggregation effect of the NFC. At pH 6 and 8, the NFC2 and 3 suspensions are similar. In this case, the consumption of the salt, revealed by EPMA-EDX characterizations, indicates that there is low or even no impact of the NaCl on the rheological properties. However, for the un-treated NFC at pH 8 a strong diminution (two orders) is observed due to the aggregation phenomenon of nanofibrillated cellulose. Regarding the pH 10 we suppose that there is a swelling of the nanofibers in these conditions, which yields the same response whatever the shear rate.

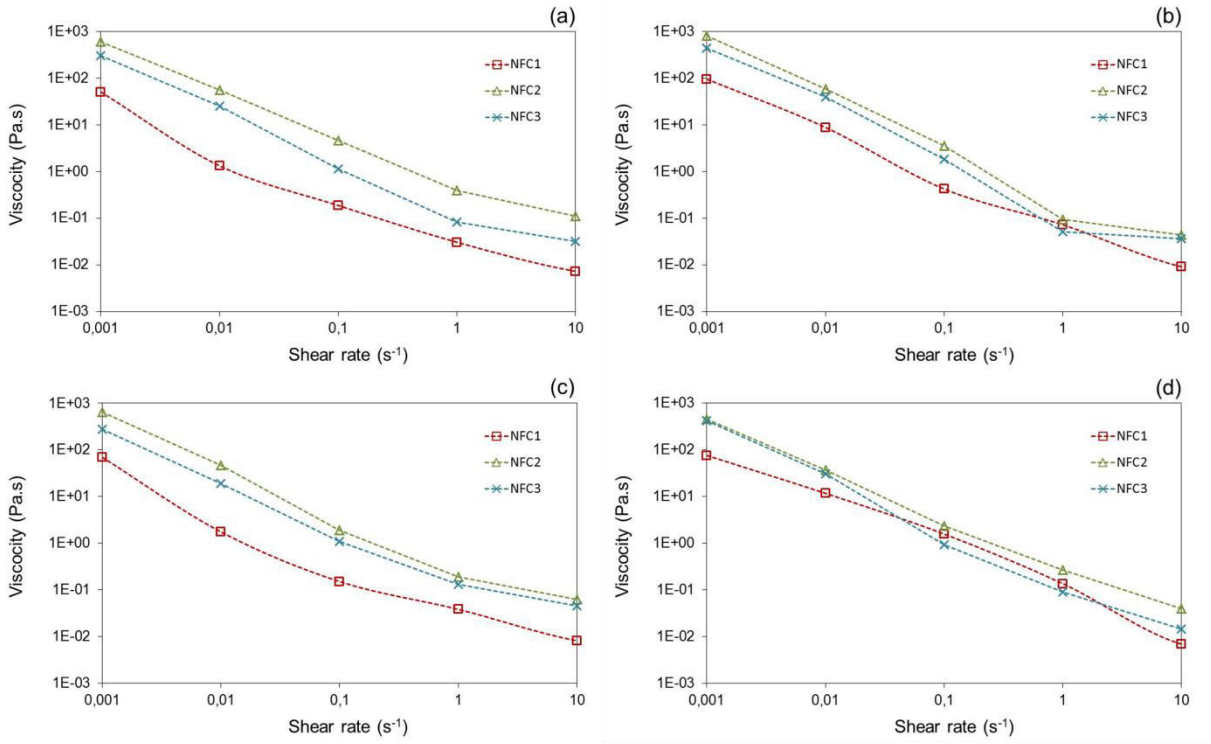

Figure 1-10 : Rheology curves – viscosity function of shear rate comparing the three samples NFC1-2-3 at each pH (a) pH 4, (b) pH 6, (c) pH 8 and (d) pH 10

In conclusion, the addition of NaCl crystals decreases the suspension viscosity, thus influencing positively the rheological properties. In one hand, crystals can decrease the viscosity at low pH (4 to 6) without affecting the structure of NFC during the process of drying, which was proved by rheological measurements on the dialyzed NFC after drying and re-dispersion steps. In other hand, NaCl crystals in good conditions of pH are very useful for the stabilization and the screening of carboxylate groups to avoid the aggregation effect.

The present study is the only one in literature dealing with a drying method of NFC in which no aggregation is observed and where such physical properties were checked after the re-dispersion like viscosity of the suspension.

1.4 Conclusion

Basing on charges present on NFC and dipole interactions between hydroxyl groups, the addition of a monovalent crystal NaCl was effective for the drying of nanocellulosic fibers thanks to the screening of these charges close to a pH value of 8 and the interactions developed between hydroxyl groups and NaCl molecules. The salt used in this paper act as a hydrogen bond blocker which limits aggregation effect observed usually for NFC once dried. To the best of our knowledge, this is the first time that nanofibrillated cellulose was completely dried and easily re-dispersed without any chemical reaction and by conserving their properties in suspension.

Acknowledgments

This research was supported by the "Scale-Up of Nanoparticles in modern PAPermaking" (SUNPAP) project of the seven framework program of European research under grant agreement n°228802. Authors thank FCBA institute (France – Grenoble) and more precisely Sandra Tapin-Lingua and Denilson Da Silva-Perez for their advices.

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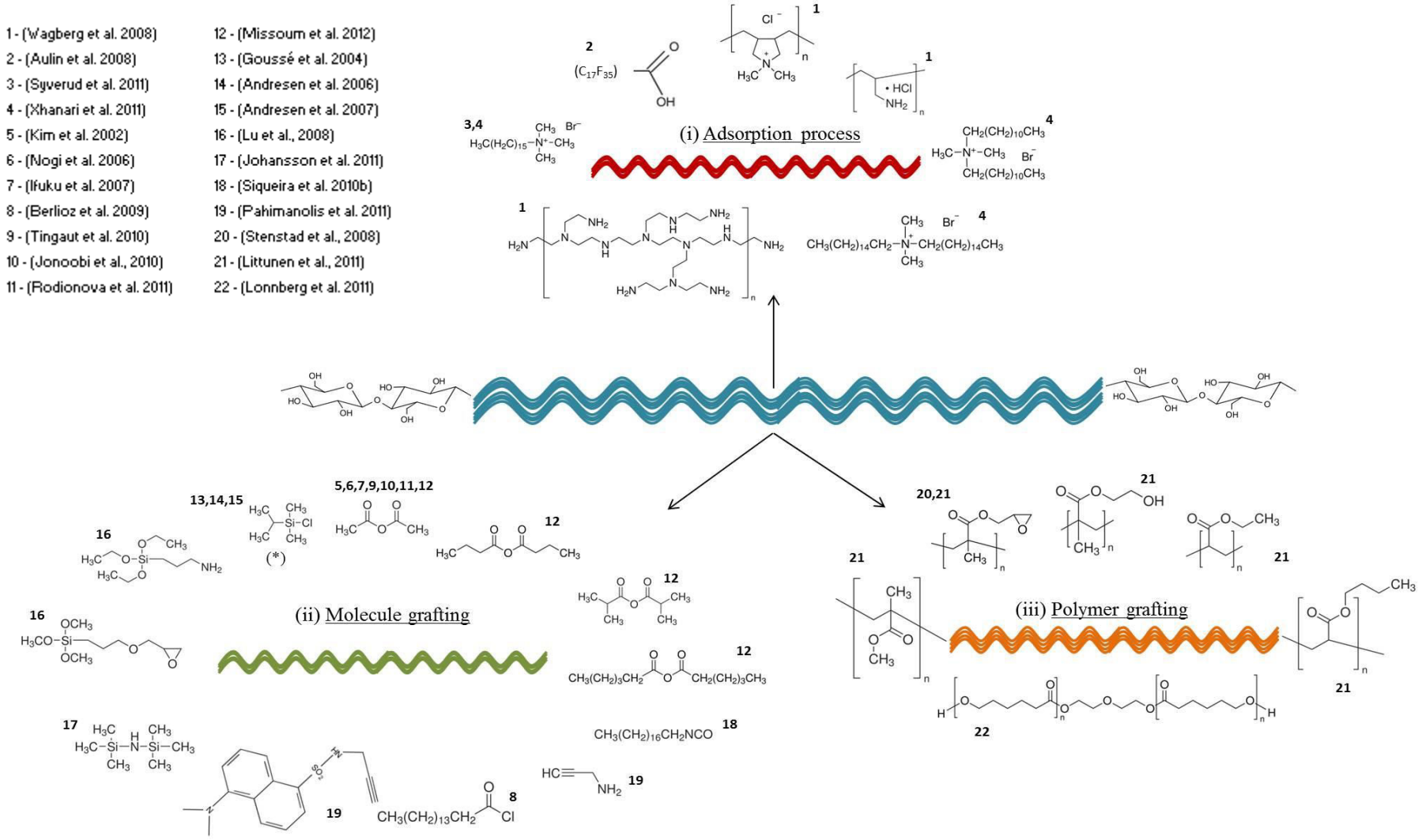
Résumé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19 - (Pahimanolis et al. 2011)
20 - (Stenstad et al., 2008)
21 - (Littunen et al., 2011)
22 - (Lonnberg et al. 2011)
(i) Adsorption process
(ii) Molecule grafting
(iii) Polymer grafting

De nos jours, des interrogations se font de plus en plus ressentir face à la diminution des matières fossiles et non renouvelable. Les besoins en ces matières ne font qu'augmenter depuis ces 10 dernières années avec l'émergence de pays maintenant industrialisés tel que la Chine ou le Brésil. Ainsi, on peut constater un intérêt croissant des politiciens, industriels et consommateurs vis-à-vis des matériaux biosourcés afin de pallier à ce manque futur.

Par exemple, les matériaux plastiques d'emballage sont majoritairement des produits issus de ressources pétrolière et donc non-renouvelables. Ainsi différents projets ont pu être financés par l'Europe afin de développer des produits innovant biosourcés (i.e. FlexpackRenew, SustainPack etc…).

Le projet SUNPAP est l'un des premiers qui a pu se focaliser sur les nanofibrilles de cellulose. L'émergence de cette nouvelle matière ces dernières années en fait un matériau très intéressante mais encore peu exploités dans l'industrie. Ainsi très peu d'applications ont pu être développés et mise en pratique au-delà d'une échelle laboratoire. Ceci est principalement due au fait qu'une production massive ne peut être actuelle proposée.

Ainsi, le projet SUNPAP s'intéresse à l'emploi de ces nanofibrilles de cellulose dans diverses applications. Par exemple le développement de papiers spéciaux utilisant des NFC et apportant une seconde fonctionnalité (papier antibactérien par fonctionnalisation des NFC). L'étude s'est donc plus focalisée sur la production de produits à forte valeurs ajoutées.

La production de nanofibrilles est maintenant bien connue et a été pour la première fois développée en 1973. Cependant, ce n'est que 20 ans plus tard que les applications de cette matière ont pu être prises en considération. Partant d'une suspension fibreuse de cellulose, cette dernière subie un traitement mécanique impliquant des forces de cisaillement considérable. La fibre est donc « pelée » en surface afin de séparer les fibres en nanofibrilles de cellulose en constituant unitaire plus fin appelé nanofibrilles de cellulose.

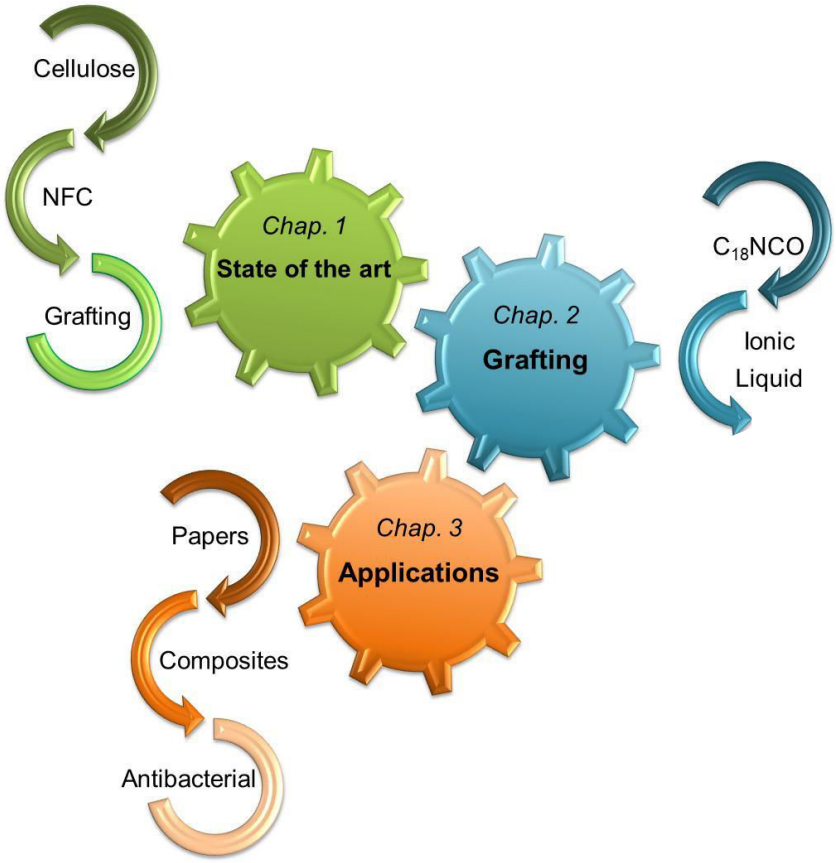
De nombreux procédés et techniques ont pu être développés afin de faciliter la production de NFC et limiter le cout de production. Ainsi le procédé étant très énergivore, on retrouve essentiellement 2 types de prétraitements sur la fibre de cellulose (i) enzymatique permettant une fibrillation plus aisée lors du traitement mécanique et (ii) oxydation TEMPO qui lui vient oxyder la fibre et la fragiliser fortement.

Les NFC présentent de nombreux avantages mais également des inconvénients. En effet, une fois produites, la surface spécifique de ce matériau est considérablement accrue ayant

pour conséquence de développer de nombreuses interactions hydrogènes. Ainsi un gel est obtenu et le taux de matière sèche classiquement atteint est compris entre 2 et 5% en poids.

Afin d'augmenter le taux de matière sèche de la suspension plusieurs méthodes peuvent être envisagées. Celles retenues dans le cadre du projet SUNPAP est la modification chimique de surface. En effet, il est important de ne pas modifier le cœur des nanofibrilles afin de conserver la morphologie fibrillaire. Dans cette optique plusieurs stratégies ont pu être étudiées dans la littérature. La Figure ci-dessous résume les trois voies de modification chimique de surface applicables et appliquées aux NFC.

Comme on peut le voir très peu de stratégies utilisent un greffage dans des conditions vertes facilitant une production à grosse échelle. Dans un but de développement plus « durable », le DoW (Description of Work) du projet SUNPAP, préconise l'emploi de solvants non toxique. Dans le cadre de cette thèse de nouvelles possibilités de greffage ont pu être considérées et plusieurs applications ont pu être étudiées. La Figure 2 reprend ainsi la stratégie adoptée tout au long de ces trois ans de thèse.



Le Chapitre 1 qui introduit plus en détails notre thématique et fait l'état de l'art des nanofibrilles de cellulose et des modifications chimique de surface réalisées, permet de

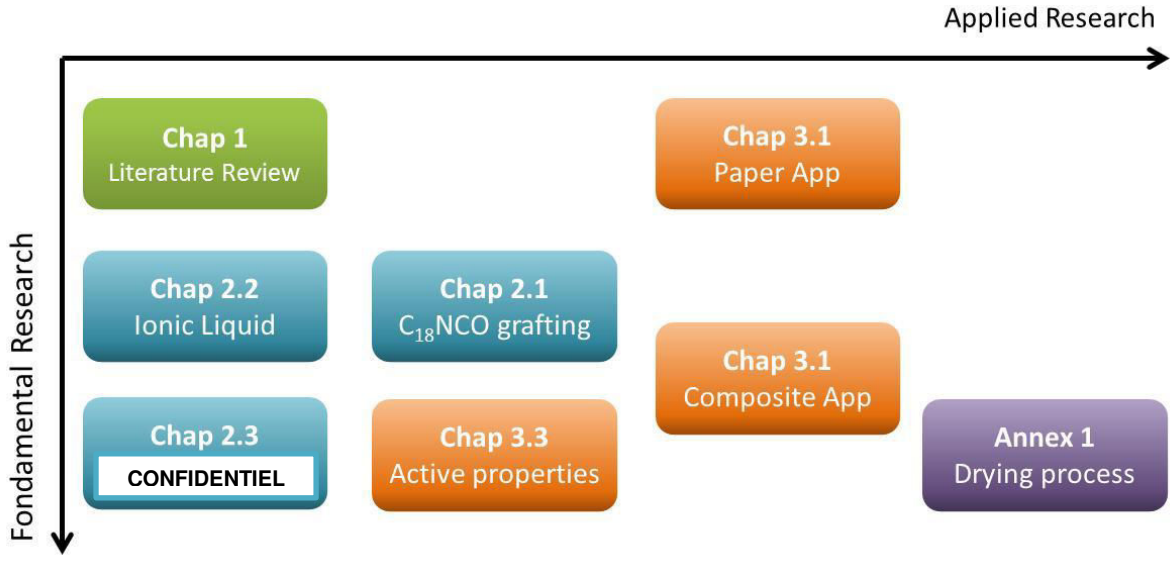
mieux identifier les différents verrous scientifiques auquel nous pourrions être confrontés lors du développement des stratégies de modifications ciblées.

Le Chapitre 2 a pour but de présenter de nouvelles stratégies de modifications dont la première partie était de se familiariser avec le greffage des NFC en se basant sur un procédé de modification maitrisé au sein du laboratoire (Article 1). Les deux autres parties se focalisent quant à elles à la réalisation d'un greffage dit « vert » afin de répondre aux attentes du projet et étant innovant. De ce fait, les liquides ioniques définis comme solvant vert et recyclable ont pu être étudiés (Article 2) ainsi qu'un greffage à base d'eau (Confidentiel).

Le Chapitre 3 évalue la possibilité d'utiliser ces NFC vierges ou modifiées dans différentes applications. Ainsi on peut retrouver des applications papetières (Article 4), composites (Article 5) ou antimicrobiennes (Article 6).

Une dernière partie placée en Annexe constitue des points de développements et d'applications qui pourraient avoir un impact non négligeable mais sortant du cadre de la modification chimique. En effet, l'annexe 1 est dédié à un procédé de séchage de ces nanofibrilles permettant leur re-dispersion après séchage qui a pu être breveté.

Chaque chapitre est constitué de 3 articles qui se rapportent à la fois à un coté appliqué mais aussi plus fondamental. La Figue ci-dessous positionne les différentes parties selon ces deux axes.



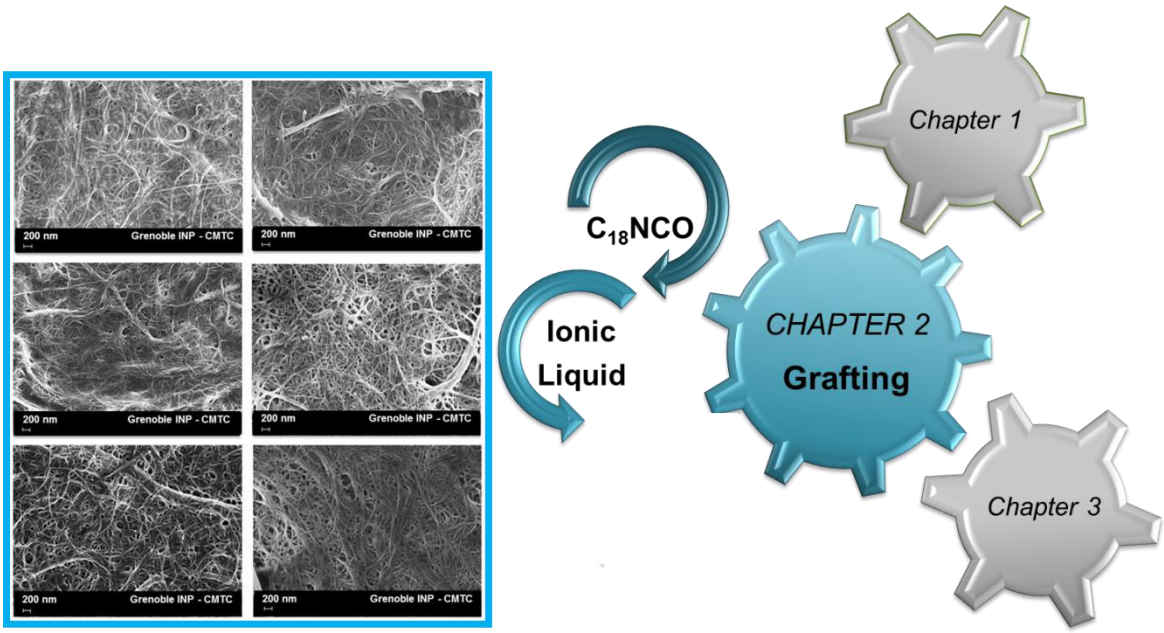
Plus en détails, le Chapitre 1 m'a permis de me familiariser avec les nanocelluloses qui m'étaient encore inconnu (NCC *vs.* NFC – Comment les produire – Caractéristiques

principales de chacun des matériaux etc…). Une fois les bases définies, nous avons pu nous intéresser plus en profondeur aux nanofibrilles de cellulose qui constituent la matière première de cette étude et plus précisément les différents moyens utilisés dans la littérature afin de pouvoir modifier physiquement ou chimiquement leurs surfaces sans pour autant altérer leur morphologie fibrillaire.

Trois voies de modifications était disponibles pour modifier les NFC pour nous focaliser sur l'un d'entre eux : le greffage de molécule. En effet, la mise en œuvre de ce type de modification chimique semble être la moins complexe pour une éventuelle modification chimique à plus grande échelle.

Les nanofibrilles de cellulose peuvent être produites selon différentes méthodes, prétraitement et sources. Une différence majeure réside entre les NFC obtenues par le biais d'un prétraitement enzymatique ou d'un prétraitement chimique TEMPO par exemple. Leur morphologie et propriétés sont compléments différentes. Il est important de noter qu'une fois produites, les suspensions de NFC dans l'eau peuvent atteindre une concentration comprise entre 2 et 5% massique. Afin d'augmenter le taux de matière sèche de ces suspensions de NFC (ce qui serait très utile pour certains procédés), la modification chimique de surface peut être envisagée comme solution.

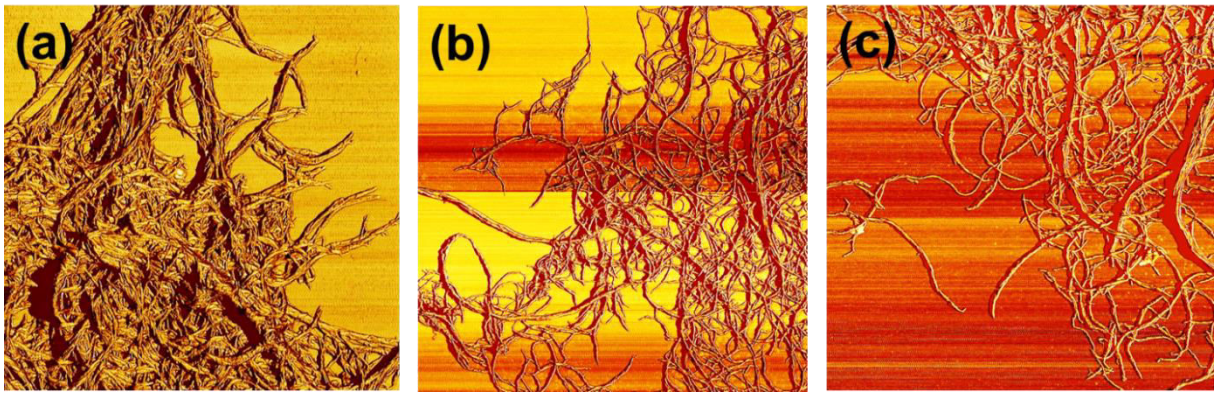
Dans ce Chapitre 2, nous avons voulu tout d'abord maîtriser le greffage de ces nanofibrilles de cellulose en contrôlant les effets de quantités de réactifs et en maîtrisant l'organisation et la caractérisation des greffons à leur surface. Ensuite nous avons souhaité proposé de nouvelles stratégies complétements innovantes en s'appuyant sur des solvants dits « verts » (les liquides ioniques) ou en proposant de greffer ces NFC en milieux aqueux.



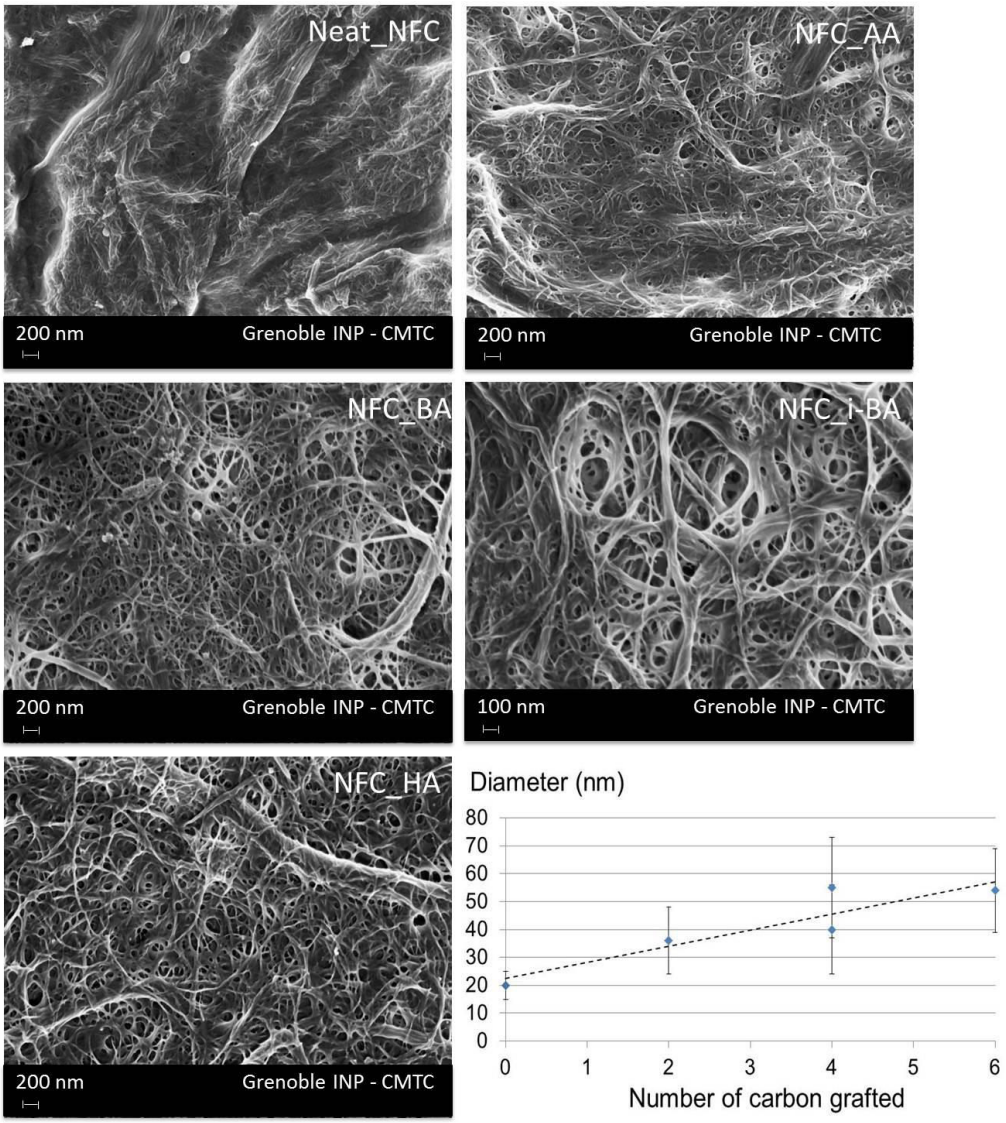
Dans la première partie de ce chapitre (**Papier 1** - Publié dans *Cellulose - 2012*), un greffage de surface des NFC a été réalisé dans différentes conditions (variation du ratio molaire entre agent de greffage et groupement hydroxyle). Le protocole ainsi établi a été adapté d'après une méthode développée au sein du laboratoire et utilisée sur les nanocristaux de cellulose et les nanofibrilles de cellulose mais avec une seule quantité de greffons. L'organisation de surface de chaînes grasses obtenues par carbanilation des NFC a ainsi pu être étudiée en détail et il a été démontrée que cette organisation influence complétement les propriétés finales des NFC.

Ces travaux montrent que les NFC peuvent être efficacement modifiées par l'emploi d'un isocyanate à chaine longue (i.e. 18 Carbones) quel que soit la quantité de greffons. La densité de greffage augmente avec l'augmentation du rapport molaire entre l'agent de greffage et le nombre de groupements hydroxyle présent à la surface de la cellulose. Grâce aux analyses XPS combinées aux analyses élémentaires des échantillons greffées, un degré de substitution interne a pu être établi pour la première fois (DSI). Il permet de quantifier les molécules greffées à la surface NFC vis-à-vis de celle qui aurait pu réagir dans la masse du matériau. L'organisation de surface de ces greffons a pu ensuite être évaluée en fonction du rapport molaire. De manière générale, les chaines aliphatiques, pour un nombre de carbone supérieur à 6-7, ont tendance à former des domaines cristallins de type cristaux liquides résultant de l'interaction latérale des chaînes aliphatiques entre elles. De ce fait, en fonction du ratio molaire utilisé lors de la réaction, des différences organisationnelles ont pu être

observées grâce aux mesures XRD. La caractérisation des propriétés physico-chimiques ont démontré la présence d'un minimum à 10eq molaire due à cette organisation de surface particulière.



Toutefois, l'inconvénient majeur de ce procédé réside dans l'utilisation de solvant assez toxique (ex : toluène) mais qui est nécessaire pour éviter les phénomènes de gonflement de la cellulose. Afin de pallier à ce problème, de nouveaux solvants verts, répondant aux mêmes critères que le toluène, ont pu être développés : les Liquides Ioniques (IL). En effet, de par leur structure menant à une pression de vapeur saturante immesurable, ces solvants n'émettent aucuns composés organiques volatiles. La deuxième partie de ce chapitre (**Papier 2** - Publié dans *Soft Matter – 2012*) démontrent l'intérêt des ILs comme nouveaux solvants pouvant modifiées la cellulose.



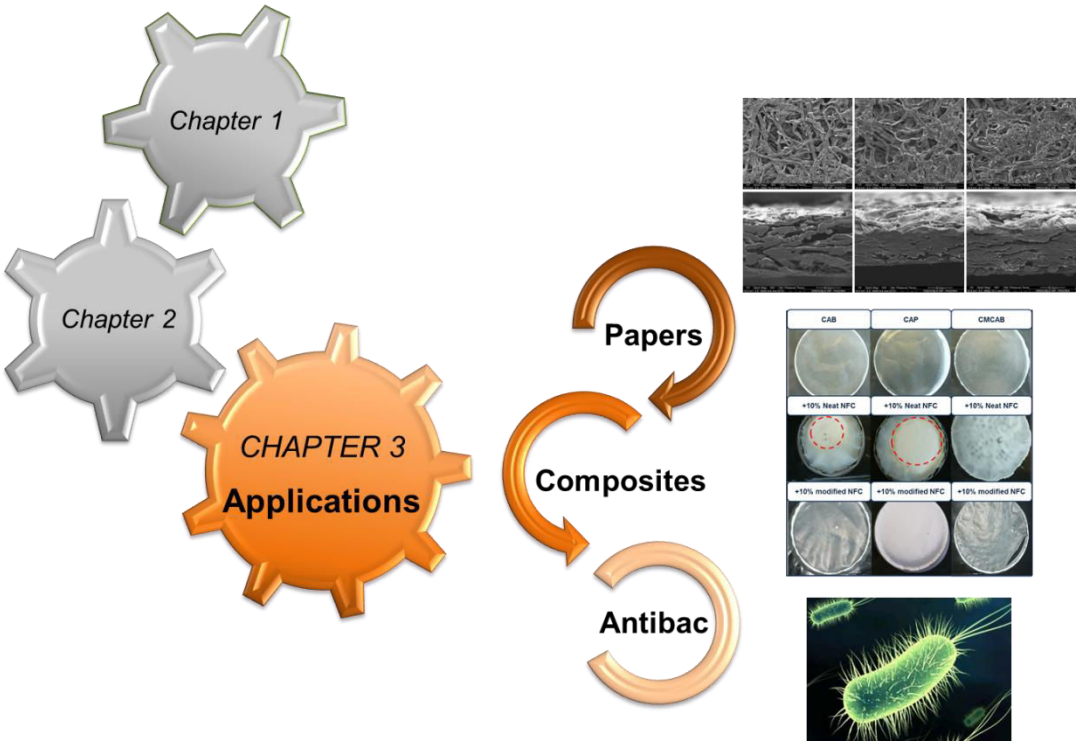
Cette étude a clairement montré que les liquides ioniques pouvaient donner lieu à un greffage efficace des NFC avec différents greffons (anhydrides) sans modifier leurs propriétés morphologiques. De plus, il a été prouvé qu'après réaction, le liquide ionique (onéreux) est recyclable et donc réutilisable pour d'autres cycles de modifications. En outre, une technique puissante d'analyse de surface (ToF-SIMS) a été utilisée pour la première fois sur des NFC pour caractériser un greffage de surface. Ces analyses confirment le greffage de surface des NFC et démontrent l'utilité de cette technique innovante.

Il s'agit de la première étude utilisant un liquide ionique comme solvant de réaction permettant une modification de surface de la cellulose en phase hétérogène. Ces résultats prometteurs pourraient donc aider à la modification chimique de plus grand volume de NFC avec des propriétés hydrophobes. Ces dernières ont pu être utilisées pour diverses applications dans le chapitre 3 suivant (composites ou matériaux antimicrobiens). Par ailleurs, nécessitant un échange de solvants, ce greffage pourraient être d'autant plus

perfectionné avec l'utilisation de NFC re-dispersable comme étudié et breveté en perspectives de ces travaux (Chapitre 4).

Malgré ces résultats prometteurs, le solvant le plus simple a manipulé (et qui évite ces échanges de solvants) reste l'eau, c'est pourquoi notre dernière stratégie s'est focalisée sur un traitement en milieu aqueux (**Confidentiel**).

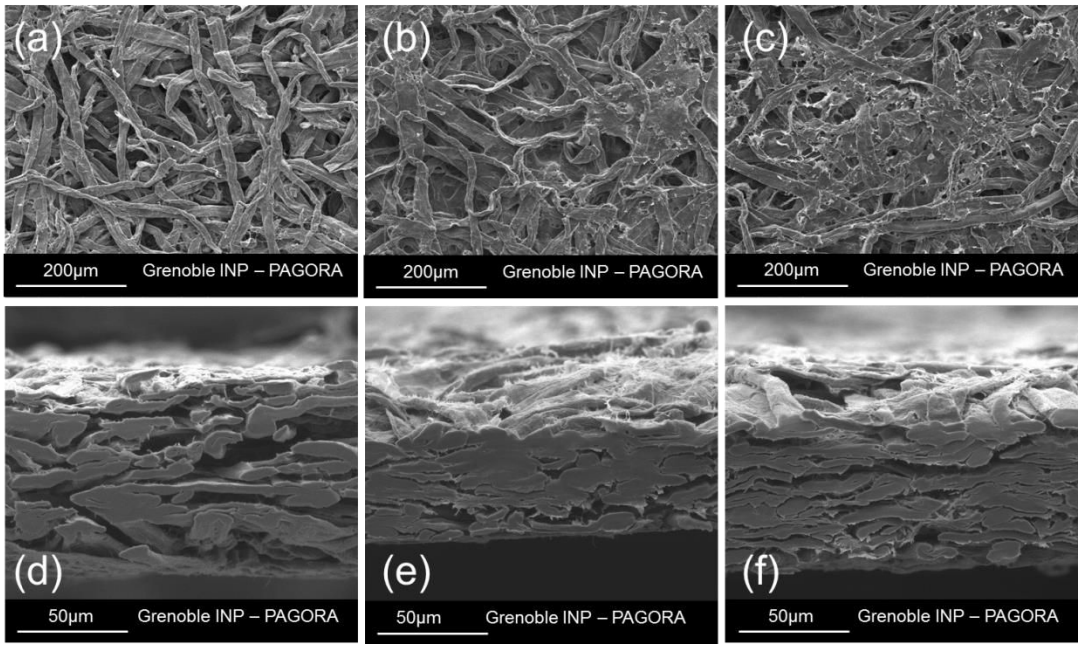
Une fois modifiées chimiquement, nous nous sommes intéressés à l'applicabilité de ces nanofibrilles de celluloses dans divers secteurs.



Comme nous venons de le voir dans le Chapitre 2, les nanofibrilles de cellulose ont été modifiées selon 3 types de greffage, sans observer de différences importantes de morphologie et structure mais avec des propriétés de chimie de surface complètement différentes.

Dans ce Chapitre 3, nous avons donc voulu utiliser et valoriser ces nouveaux types de NFC dans 3 champs d'applications distinctes : dans le domaine du papier, celui des composites et enfin celui des matériaux antimicrobiens.

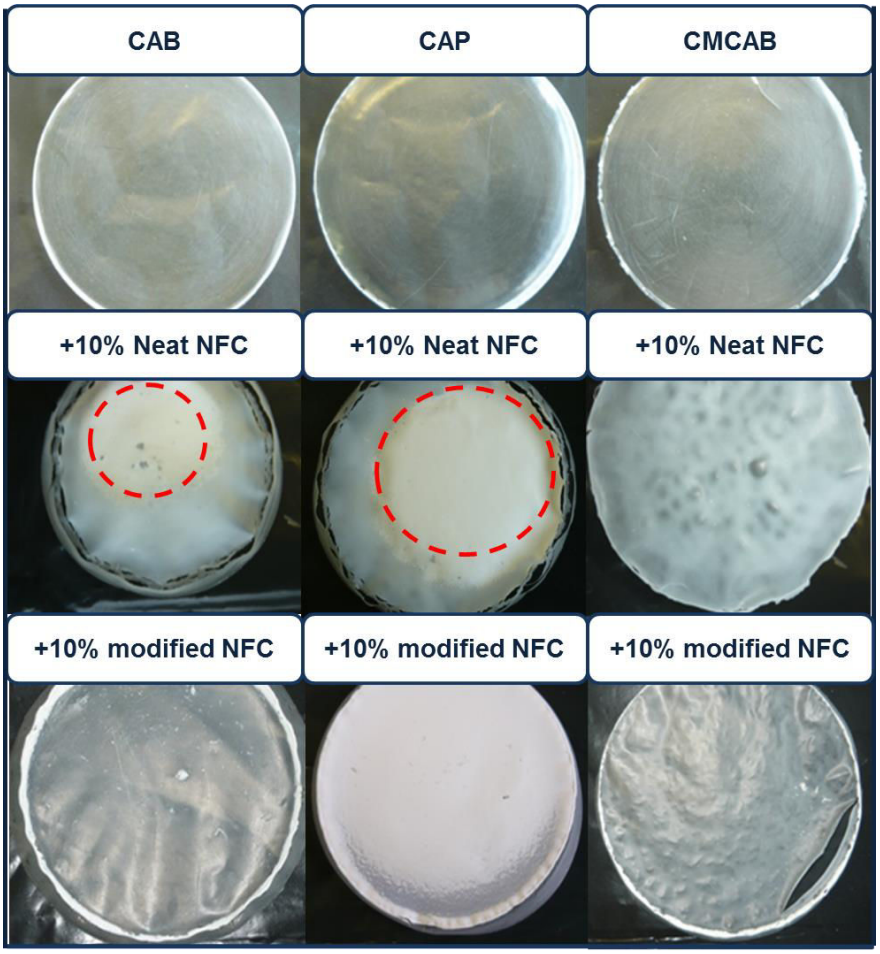
Dans la première partie de ce chapitre (**Papier 4** - *Soumis dans Material Chemistry and Physics - 2012*), les NFCs greffées ont été introduites en masse dans du papier à différents ratio massique. L'objectif de cette étude est à la fois d'augmenter les propriétés mécaniques du matériau mais également de conférer au papier un caractère hydrophobe.



L'un des points importants de cette étude réside dans la quantification de la rétention réelle des NFC (modifiées ou non) dans le matelas fibreux. Les caractérisations du complexe « fibres de cellulose/NFC », ont montré l'intérêt d'utiliser des nanofibrilles de cellulose afin de renforcer les propriétés mécaniques du papier. De plus, les NFC modifiées apportent, elles, clairement un plus avec le renfort mécanique mais aussi un comportement hydrophobe.

Afin de développer des applications à hautes valeurs ajoutées, il a été décidé d'utiliser les nanofibrilles modifiées par la stratégie employant les liquides ioniques dans les composites. La deuxième partie de ce chapitre (**Papier 5** - Soumis dans *Composites Part A: Applied Science and Manufacturing – 2012*) est donc dédiée à l'utilisation de nanofibrilles de cellulose modifiées dans une matrice de dérivé de cellulose pour créer un monomatériau cellulose en favorisant un continuum à l'interface renfort/matrice.

Pour ce faire, 3 dérivés cellulosiques : CAB – CAP – CMCAB, ont été étudiées. L'idée première était d'utiliser les NFC modifiées disposant de greffons de faible longueur en carbone (C_2, C_4 et C_6) pour maximiser la compatibilité entre la matrice et les éléments de renfort.



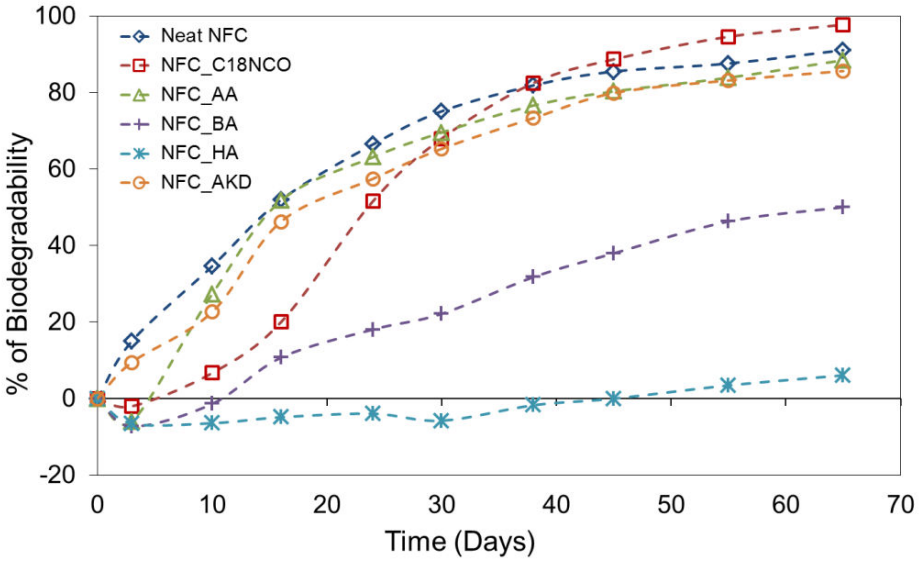
En effet, un composite entièrement fait de matériaux issus de ressources renouvelables a été préparé. L'emploi de NFC dans des matrices de dérivés de cellulose a permis d'augmenter de manière significative les propriétés thermomécaniques des bionanocomposites. L''ajout de 10% massique de NFC natives ou modifiées permet d'augmenter le plateau caoutchoutique de 10 à 30°C selon le type de matrices ou éléments de renforts utilisés. Il est important de noter que la dispersion des NFC modifiées conduits à un film beaucoup plus homogène que ceux obtenus avec des NFC vierges mais avec des renforts légèrement plus faibles. Ainsi on a pu montrer dans cette étude que plus le réseau est structuré par des liaisons hydrogènes, plus les propriétés thermomécaniques sont augmentées.

Nous avons donc pu également étudier l'impact de ces NFC modifiées en tant qu'agent antibactérien et suivre dans un second temps la biodégradabilité de ces éléments (**Papier 6**)

Cette étude montre pour la première fois des résultats très intéressants et prometteurs qui pourrait être utilisés dans des applications à fortes valeurs ajoutées. En effet, il est démontré

que les NFC modifiées peuvent être considérées, comme des agents antibactériens (ou au moins bactériostatique) tout en conservant leurs propriétés de biodégradabilité.

Les traitements chimiques appliqués sur les NFC ont permis de développer une activité antibactérienne vis-à-vis de bactéries de type Gram+ ou Gram-. Cet effet peut varier en fonction du greffon. Qui plus est, une certaines synergie lorsque des nanoparticules de TiO_2 sont ajoutées, a été démontrée.



La biodégradabilité des échantillons a ensuite été testée. Selon le type de greffage, on peut conserver ou contrôler la biodégradabilité du matériau final. Une telle étude ouvre un large spectre d'application et devrait être complétée par d'autres types de greffage et en étudier l'impact dans un matériau final.

Ce chapitre 3 propose donc une avancée significative dans les applications de nanofibrilles de cellulose modifiées avec des résultats prometteurs fonction des différentes stratégies utilisées pour la modification chimique. Comme précédemment exposé, les nanofibrilles de cellulose constituent donc un matériau innovant avec une large palette d'application. Certains effets peuvent être ainsi contrôlés et on peut en adapter les propriétés finales une fois dans un matériau.

En Conclusion les nanofibrilles de cellulose sont un matériau facilement exploitable dans l'industrie, soit dans sa forme vierge soit modifiés chimiquement afin d'adapter ses propriétés. Les NFC s'intégreront donc aisément dans les process industriels existant.

Les nanocelluloses connaissent un fort développement depuis ces dernières décennies et font l'objet de nombreuses études menées par les industriels et/ou consortiums académiques. Cette étude s'insère dans le cadre d'un projet européen (SUNPAP) visant à l'industrialisation des nanofibrilles de cellulose (NFC). La présente thèse fait l'état de nouveaux procédés de modification chimique de surface des NFC dans une optique de chimie verte. Plusieurs stratégies ont été développées telle que l'emploi de liquides ioniques comme solvant de réaction (décrit comme solvants verts) ou l'utilisation d'une nanoemulsion en phase aqueuse permettant le greffage de surface des NFC. Dans le but d'étudier l'impact de ces modifications chimiques, les substrats ainsi traités ont été par la suite utilisés dans diverses applications. Ainsi, des bionanocomposites ont pu être produits, l'impact sur l'introduction de NFC (modifiées ou non) dans du papier a également été étudié. Une étude sur les propriétés antibactériennes et la biodégradabilité des NFC modifiées est également proposée. Une caractérisation approfondie des NFC vierges et modifiées a été réalisée. Des techniques puissantes et innovantes ont été utilisées pour caractériser ces substrats tels que l'XPS (X-ray Photoelectron Spectroscopy) ou encore la SIMS (Secondary Ion Mass Spectrometry). Toutes ces modifications, applications et caractérisations proposées constituent une avancée et des perspectives prometteuses dans le monde des nanocelluloses.

Nanocelluloses know a strong interest since last decades and they are the subject of many studies led by industrials and / or academic consortia. This study is a part of a European project (SUNPAP) for the industrialization of nanofibrillated cellulose (NFC). This thesis is the state of new methods for the chemical surface modification of NFC with a view of green chemistry. Several strategies have been developed such as the use of ionic liquids as reaction solvent (described as green solvents) or the use of an aqueous medium in order to graft the surface of NFCs. Thus, the treated substrates were then used in various applications. Also, bionanocomposites were produced, the impact of the introduction of NFC (modified or not) in paper sheets has also been studied. A study on the antibacterial properties and biodegradability of modified NFC is also proposed. Several characterizations of neat and modified NFC were performed. Powerful and innovative techniques have been used to characterize these substrates such as XPS (X-ray Photoelectron Spectroscopy) or SIMS (Secondary Ion Mass Spectrometry). All these chemical modifications, applications and characterizations are offered promising prospects in the world of nanocelluloses.